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**NANYANG
TECHNOLOGICAL
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**ADVANCED AIR ELECTRODES FOR
SOLID OXIDE ELECTROLYZER CELLS**

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ABSTRACT

Solid oxide electrolyzer cells (SOECs), which serve as a highly efficient and viable technology for energy conversion and storage, have drawn great attention in the recent years, especially with the continuous rise of renewable energy usage. However, the high degradation rate hinders the commercialization of this technology. One of the sources of degradation is the air electrodes. Therefore, it is urgent to understand the degradation mechanism of air electrodes and then to develop methods to improve the stability of SOECs. At present, LSCF ($\text{La}_{1-x}\text{Sr}_x\text{Co}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$)-based air electrodes are under intensive research and selected as the air electrode used in this thesis, as the traditional LSM (Sr-doped Lanthanum Manganese Oxide)-based air electrodes usually suffer severely from poor electrochemical activity and tendency to delaminate from YSZ (Yttria Stabilized Zirconia) electrolytes. This thesis gives an in-depth investigation on the degradation mechanism during fabrication and operation of LSCF electrodes in SOECs, and possible solutions to suppress the degradation.

Firstly, possible interfacial reactions between LSCF and YSZ during the fabrication stage were investigated. It was found that SrZrO_3 second phase can be generated, along with the precipitation of $(\text{CoFe})_3\text{O}_4$ spinel phase, by sintering YSZ and LSCF powder mixture for 2 h at a sintering temperature of 850 °C or higher. This SrZrO_3 second phase can cause substantial increase of the polarization resistance, R_p , of the LSCF electrodes on YSZ electrolytes obtained under open circuit voltage (OCV), from $0.03 \, \Omega \, \text{cm}^2$ to $2.72 \, \Omega \, \text{cm}^2$ with the increase of the sintering temperature from 800 °C to 1000 °C. By scanning electron microscope (SEM), a thin but dense layer of SrZrO_3 was

observed covering the whole surface of YSZ electrolyte when LSCF was sintered at 1000 °C, most likely to be a result of the high diffusivity of Sr. Furthermore, it was found that the SrZrO₃ second phase caused more severe performance drop in fuel cell mode than in electrolyzer mode.

Secondly, the degradation mechanism of LSCF air electrodes during high-temperature anneal under OCV was investigated. It was found that the increase of R_P of LSCF under OCV condition showed a linear dependence on the square root of time, indicating diffusion processes. A comparison between the behaviour of the sample before and after nitric acid etching treatment, which can remove the possible surface precipitated substances, showed that the performance has been improved and the degradation rate has been reduced after nitric acid etching treatment. Given that, the degradation is most likely due to the emergence of surface inhibited species on the LSCF electrode, which can be removed by nitric acid treatment. XPS examination showed that the “surface” Sr increased upon the annealing time and decreased upon the nitric acid etching treatment. Consequently, it can be concluded that the degradation of LSCF electrodes under OCV is caused by the surface segregation of Sr-based species. This confirms the detrimental role of surface segregated Sr-based phase on the electrochemical performance of LSCF electrodes.

After that, LSCF electrodes on YSZ electrolytes were applied with electrolysis current. During the test at 800 °C, it was found that the applied electrolysis current could suppress the degradation or even activate the electrode. For instance, the R_P of the LSCF electrode sintered on the YSZ electrolyte at 1000 °C decreased from 1.53 to 0.59 $\Omega \text{ cm}^2$ after the application of electrolysis current of 1 A cm^{-2} for 24 h at 800 °C. However, after

electrolysis test for 24 h, the LSCF electrode was found delaminated from the YSZ electrolyte. Subsequently, the activation and delamination behaviour was thoroughly studied. As revealed by SEM images, the SrZrO_3 layer developed during fabrication stage was found to delaminate from the YSZ electrolyte rather than that the LSCF electrode delaminated from the SrZrO_3 layer. Moreover, Co diffusion into the SrZrO_3 layer was detected by energy dispersive x-ray and later proven to be able to improve the catalytic activity of the SrZrO_3 layer. Then, the catalytic activity of the SrZrO_3 layer could render the generation of oxygen at the SrZrO_3 –YSZ interface. However, owing to the low porosity of the SrZrO_3 layer, the generated oxygen cannot diffuse out effectively and accumulated at the interface. Eventually, the bonding was weakened and the delamination of the SrZrO_3 layer took place. This finding indicates that to improve the durability of LSCF electrodes, it is critical to prevent the formation of SrZrO_3 second phase and Co diffusion during the fabrication and operation of SOECs.

At last, a half-cell with a dense GDC interlayer, which can prevent the formation of SrZrO_3 , was tested for 264 h under 1 A cm^{-2} electrolysis current at 800°C . No delamination of the LSCF electrode was found after the test. By comparison, another half-cell with a porous GDC interlayer, which cannot fully prevent the formation of SrZrO_3 second phase, was also fabricated and tested under the same condition. Detachment was again found at the interface between the SrZrO_3 phase and the YSZ electrolyte. This result validates the above proposed mechanism and proves the effectiveness of the dense GDC interlayer in preventing the delamination problem. The half-cell with dense GDC interlayer will be used for future study.

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LIST OF ABBREVIATIONS & SYMBOLS

Abbreviations

ADIS	Analysis of Differences in Impedance Spectra
AC	Alternating Current
AEC	Alkaline Electrolyzer Cell
AH	Absolute Humidity
CNLS	Complex Nonlinear Least Squares (Approximation for EIS curve fitting)
CPE	Constant Phase Element
CVD	Chemical Vapour Deposition
DRT	Distribution of Relaxation Times
DC	Direct Current
EDX	Energy Dispersive X-ray Spectroscopy
EGR	Exhaust Gas Recycling
EIS	Electrochemical Impedance Spectroscopy
FESEM	Field Emission Scanning Electron Microscopy
FFT	Fast Fourier Transform
HHV	Higher Heating Value
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
LHV	Lower Heating Value
MIEC	Mixed Ionic and Electronic Conductor
OCV	Open Circuit Voltage
PEMEC	Proton Exchange Membrane Electrolyzer Cell
SOEC	Solid Oxide Electrolyzer Cell
SOFC	Solid Oxide Fuel Cell
SOC	Solid Oxide Cell
TPB	Triple Phase Boundary
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction

Symbols

<i>E</i>	Voltage
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LIST OF ABBREVIATIONS & SYMBOLS

E_a	Activation Energy
f	Frequency
f^0	Summit Frequency
F	Faraday Constant
I – V curve	Current–Voltage Curve (DC polarization curve)
L	Inductance
n	Frequency Power
p	Partial Pressure
Q	Heat Energy Demand
R_p	Polarization Resistance
R_s	Ohmic Resistance
T	Temperature
Y	Admittance
Z'	Real Axis of Nyquist Plot
Z''	Imaginary Axis of Nyquist Plot
ω	Angular Frequency
ΔC_p	Heat Capacity at Constant Pressure
ΔG	Gibbs Free Energy or Electrical Energy Demand
ΔH	Enthalpy Change
ΔS	Entropy Change

Subscripts & Superscripts

0	Standard or Equilibrium
H	High-Frequency Process
L	Low-Frequency Process

Chemicals

Ba	Barium
BCFN	$\text{Ba}_{1-x}\text{Co}_y\text{Fe}_z\text{Nb}_{1-y-z}\text{O}_{3-\delta}$
Ce	Cerium
Co	Cobalt
Fe	Iron
Ga	Gallium
Gd	Gadolinium
GDC	Gadolinium-doped Ceria ($\text{Gd}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$)

LIST OF ABBREVIATIONS & SYMBOLS

H ₂	Hydrogen
H ₂ O	Water
La	Lanthanum
LSCF	La _{1-x} Sr _x Co _y Fe _{1-y} O _{3-δ}
LSGM	La _{1-x} Sr _x Ga _y Mg _{1-y} O _{3-δ}
LSM	La _{1-x} Sr _x MnO _{3-δ}
Mg	Magnesium
Mn	Manganese
Nb	Niobium
Pt	Platinum
SDC	Samarium-doped Ceria (Sm _x Ce _{1-x} O _{2-δ})
Sr	Strontium
YSZ	Yttria-stabilized Zirconia

LIST OF ABBREVIATIONS & SYMBOLS

Chapter I Introduction

1.1 Backgrounds

As of today, the constant use of fossil fuel has already caused environmental problems such as greenhouse effect, and will eventually lead to the depletion of the natural resources (Chiari et al., 2011; Höök et al., 2013; Hoel et al., 1996; Rimos et al., 2014; Shafiee et al., 2009; Zecca et al., 2010). Moreover, heavy dependence on fossil fuels also threatens the energy security (Ellabban et al., 2014; Mathews et al., 2014). In order to tackle these problems, renewable energy like solar and wind energy must be sought. However, renewable energy is site-specific and intermittent by nature. Thus, energy storage and re-distribution is of great importance to balance the supply and the demand. Till now, several methods to store the excess renewable energy have been studied, including flywheel storage (Mousavi G et al., 2017), pumped hydro storage (Rehman et al., 2015), pressurized air storage (Succar et al., 2008), battery storage (H. Chen et al., 2009; Dunn et al., 2011), supercapacitor storage (Yan et al., 2014) and hydrogen storage (Sakintuna et al., 2007). The working principles of these technologies are briefly introduced below and Table I-1 compares the characteristic parameters of different technologies (Akorede et al., 2010; Beaudin et al., 2010; Fuchs et al., 2012; Hadjipaschalis et al., 2009; Ibrahim et al., 2008).

Flywheel storage: A flywheel is an energy storage device which can store the excess energy into the kinetic energy of a mass rotating round an axis with high speed.

Pumped hydro storage: The excess energy is stored in the form of the potential energy of water in a higher reservoir. The water is released back into the lower reservoir to generate electricity when there is a high demand.

Pressurized air storage: Air is pumped into a sealed underground cavern to a high pressure during off-peak hours. The pressurized air is then kept underground for peak use.

Battery storage: Storage batteries are rechargeable electrochemical systems used to store energy in the form of chemical energy. There are a few types of batteries that can be used as energy storage batteries, Lithium-ion battery, flow battery and Lead-acid battery.

Supercapacitor storage: Supercapacitors are very high surface areas activated capacitors that use a molecule-thin layer of electrolyte as the dielectric to separate charge. Energy storage is by means of static charge.

Hydrogen storage: Storing electrical energy in the form of hydrogen energy. The hydrogen can be generated via a few routes, including methane reforming, thermochemical water splitting, photocatalytic water splitting or water electrolysis (Berg et al., 2016; M. A. Laguna-Bercero, 2012; Lei et al., 2016; Mo et al., 2016; M. Ni et al., 2008; Yanwei Zhang et al., 2013). The generated hydrogen can be stored in high-pressure tank or in the form of metal hydride.

From Table I-1, it can be seen that all the methods have their own deficiencies. For instance, pressurized air and pumped hydro require appropriate geographical regions. A flywheel suffers from severe self-discharge which limits its application to transient conditions. For batteries and supercapacitors, although the self-discharge rate is not as high as flywheel, they are still not suitable for long-term storage. In addition, due to the relatively low energy density, high capital costs are required for large scale energy storage. As for energy storage in the form of hydrogen, the round-trip efficiency is low, only 40% if co-generated heat of the fuel cell operation is not considered and this value may reach 60% if the heat is included.

Table I-1 Comparison of the characteristic parameters between different energy storage technologies

Energy storage technologies	Flywheel ¹	Pressurized air	Pumped hydro	Li-ion battery	Pb-acid battery	Hydrogen	Supercapacitor ²
Power density (W/kg)	<1000	50–300 MW/system	>10 GWh/system	500–2000	180	800–1000 ³	10,000
Energy density (Wh/kg)	<100	30–60	0.5–1.5	80–150	30	400–1500	<5
Lifetime	<1,000,000 cycles 20 years	20–100	40–100	>1500 cycles	1200–1800 cycles 5–15 years	30 years	~500,000 cycles <12 years
Round-trip Efficiency	90%	40–80%	75–82%	83–86%	85–90%	40% ⁴	97%
Self-discharge	20%/h	15–30%/month	0.15–0.6%/month	5%/month	2%/month (25 °C)	0.09–0.9%/month	14%/month
Site-specific?	No	Yes	Yes	No	No	No	No
Environmental concerns	Low	Lacking	Lacking	High	High	Very low	High
Cost (\$/kWh)	400–800	2–50	5–100	600–2500	50–100	2–20 ⁵	300–2000
Reference	(Ehteshami et al., 2014; Fuchs et al., 2012; Ibrahim et al., 2008; Klell, 2010)						

1. Data used is for flywheel with composite materials.

2. Data used is for electrochemical double layer supercapacitors.

3. Data used is for fuel cells operated on hydrogen.

4. Co-generated heat by fuel cells are excluded in the calculation of round-trip efficiency.

5. Does not include the cost for producing hydrogen and converting hydrogen into electricity.

However, the purpose of using renewable energy is to mitigate the negative environmental impacts of traditional fossil fuels and to strengthen the energy security. From these two perspectives, storage of energy in the form of hydrogen has some advantages over the other options. Firstly, hydrogen is a potential alternative fuel, which can serve all the purposes, as well as a preferred energy carrier for the future (Ehteshami & Chan, 2014). By comparison, the other energy storage methods can only generate electricity. Secondly, hydrogen is environmentally benign. As for batteries and supercapacitors, their environmental impacts are one of major concerns. Thirdly, the energy conversion device and energy storage device are separate when hydrogen is used as the energy carrier. That is, the energy conversion capacity and energy storage capacity can be considered and designed separately. However, the energy carriers of other energy storage devices are the devices themselves. Due to the limited energy density of these devices, the volume required to store a certain amount of energy is large. For instance, hydrogen possesses an energy density as high as 0.4 kWh/kg in a steel tank, 1.5 kWh/kg in a carbon fibers reinforced tank (Klell, 2010) or 0.58 kWh/kg (Zittel et al., 1996) in the form of metal hydride, while the energy density for a lithium-ion battery is only 0.112 kWh/kg (Majeau-Bettez et al., 2011). Therefore, the high energy density of hydrogen makes the storage of it materials-saving and environmentally friendly. Last but not least, the self-discharge of hydrogen is the lowest, except for pumped hydro which requires a specific geographical feature. Thus, it is almost the only option to store the energy in the long term as back-up energy to strengthen the energy security.

Hydrogen can be produced from water by thermochemical water splitting, photocatalytic water splitting or water electrolysis (Berg et al., 2016; M. A. Laguna-Bercero, 2012; Lei et al., 2016; Mo et al., 2016; M. Ni et al., 2008; Yanwei Zhang et al., 2013). Among those methods, water electrolysis possesses the highest efficiency, up to a system efficiency of 70% (Dincer et al., 2015; Holladay et al., 2009; M. Wang et al., 2014). Currently, several kinds of electrolyzer systems have been developed, which can be classified into three main types in terms of the electrolyte material of the cell used: alkaline electrolyzer cell (AEC), proton exchange membrane (polymer) electrolyzer cell (PEMEC) and solid oxide electrolyzer cell (SOEC). Table I-2 compares the characteristics of the three different electrolyzer cells.

Table I-2 Comparison of characteristics between the different electrolyzer cells

Technology	AEC, large-scale	PEMEC	SOEC
Status	Commercial	Pre-commercial	Prototype
Electrolyte	Potassium hydroxide	Ion exchange membrane	Solid oxide
Operating Temperature	70-90 °C	80-150 °C	600-1000 °C
Charge Carrier	OH ⁻	H ⁺	O ²⁻
Electrolyte State	Immobilized liquid	Hydrated solid	Solid
Cell Hardware	Carbon/metal-based	Carbon/metal-based	Ceramic
Electrodes	Transition metals	Carbon	Ceramic/Metal cermet
Catalyst	Platinum	Platinum	Electrode material
Fuel	H ₂ O	Pure H ₂ O	H ₂ O _(g) , CO ₂
Electrical Efficiency (% LHV of H ₂)	56-69	56-83	86-119*
References	(Cifraín et al., 2004; Gülzow, 1996; <i>International Energy Agency 2014 Annual Report</i> , 2014)	(<i>International Energy Agency 2014 Annual Report</i> , 2014; Litster et al., 2004; Sishtla et al., 1998)	(Gardner et al., 2000; <i>International Energy Agency 2014 Annual Report</i> , 2014)

*: Heat supplied was not calculated and thus the electrical efficiency can be higher than 100%, which will be detailed in the next chapter.

From Table I-2, it can be seen that although SOEC is the least commercial one to electrolyze water among the three types of electrolyzers, it bears the highest electrical efficiency due to the high operating temperature. With its capability of utilizing industrial waste heat to replace electricity for H₂ production, an SOEC consumes only 28–39 kWh electricity to produce 1 kg hydrogen (Henke et al., 2014). Therefore, SOECs are now under intensive research on the grounds that it can convert the renewable energy or excess energy into hydrogen with high efficiency (Akikur et al., 2014; Gómez et al., 2016; Joneydi Shariatzadeh et al., 2015; M. A. Laguna-Bercero, 2012; Lei et al., 2016; M. Ni et al., 2008; Sigurvinsson et al., 2007; Stempien et al., 2013; Zhou et al., 2016). Besides, it can be operated reversely as solid oxide fuel cells (SOFCs) with the stored hydrogen for combined heat and power co-generation with a total efficiency as high as 90% (Buonomano et al., 2015; Qu et al., 2016). Thus, renewable energy combined with a reversed solid oxide cell (RSOC), which can be operated either in electrolyzer mode or in fuel cell mode, is one of the most promising methods to achieve a more sustainable future.

1.2 Problem statements

One critical issue associated with SOECs is its high degradation rate before the commercialization of this technology can take place (Knibbe, Traulsen, et al., 2010; Mawdsley et al., 2009; Schefold et al., 2015b; Tietz et al., 2013). One of the sources of degradation comes from the air electrode. For traditional $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$ (LSM)-based electrodes, failure mechanism like interfacial reaction with electrolytes, A-site element segregation and delamination of electrode from electrolytes were reported in the previous

literatures (Mawdsley et al., 2009; Ortiz-Vitoriano et al., 2013; Tietz et al., 2013). Thus, materials to replace LSM are desperately needed.

Currently, $\text{La}_{1-x}\text{Sr}_x\text{Co}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$ (LSCF) is of great interest as a potential anode, or air electrode, material for SOECs to replace traditional LSM electrode (Choi et al., 2013; Miguel A. Laguna-Bercero et al., 2010; M. A. Laguna-Bercero et al., 2011). As a mixed ionic and electronic conductor (MIEC) with high catalytic activity, LSCF performs much better than LSM as cathode in SOFC (Dumaisnil et al., 2014; Esquirol et al., 2004; Fu et al., 2008; Kan et al., 2009). Besides, the ionic conductivity of LSCF is believed to be able to mitigate the above-mentioned delamination phenomenon (Moçoteguy et al., 2013).

However, several groups have characterized LSCF as air electrode in both SOFC and SOEC and reported that LSCF also encountered its own problems which can jeopardize the stability of SOECs. Firstly, the interfacial reaction between LSCF and YSZ (Yttria stabilized zirconia), which is the most commonly used electrolyte for SOEC, is more severe than the reaction between LSM and YSZ (Kindermann et al., 1996; Stochniol et al., 1995). Secondly, the Sr surface segregation of LSCF may have serious negative effect on the performance (W. Araki et al., 2016; Wakako Araki et al., 2014; Cai et al., 2012; H. Ding et al., 2013; John Druce et al., 2014; Fister et al., 2008; Jung et al., 2012; Kubicek et al., 2013; Kubicek et al., 2011; W. Lee et al., 2013; Oh et al., 2012; Van Der Heide, 2002). Thirdly, the delamination of LSCF air electrodes was also observed (Fan, Keane, Singh, et al., 2014; Hjalmarsson et al., 2013; S. J. Kim et al., 2013; Kim et al., 2014).

1.3 Objectives

In this study, LSCF is selected as the air electrode material due to its better performance than traditional LSM electrodes. However, to enable the practical application of SOECs, improving the stability of LSCF air electrodes is of great importance. Before that, a thorough understanding on the degradation mechanism is needed. Although above problems of LSCF electrodes have been reported, a thorough characterization and investigation on LSCF electrodes in SOECs is still lacking. Thus, the exact effects of these problems of LSCF electrodes on the stability of SOECs are unclear. Consequently, below statements, which consist of the objectives of this study, needs to be investigated:

- To inspect the interfacial reaction between LSCF and YSZ and its effect on the electrochemical performance.
- To understand the degradation mechanism of LSCF air electrodes during high-temperature anneal.
- To study the electrochemical behaviours of LSCF air electrodes under electrolysis current.
- To investigate the mechanism for the delamination of LSCF air electrodes.
- To develop a method to prevent the delamination of LSCF air electrodes.

1.4 Scope and Dissertation Overview

The scope of this research is outlined below:

- *Investigation of the reaction between LSCF and YSZ and its effect on the electrochemical performance (Chapter IV)*

The chemical compatibility between the electrode and the electrolyte is of great importance in increasing the electrochemical performance and the stable operation of an SOEC. Therefore, this part of the work aims to study the possible reactions between LSCF and YSZ both in the power mixture and in the fabrication condition of half-cells. The possible reaction products were identified and the morphological changes caused by the interfacial reaction between LSCF electrodes and YSZ electrolytes were observed. The effect of the interfacial reactions on the electrochemical performance of LSCF electrodes were recognized.

- *Investigation of the degradation mechanism of LSCF electrodes under OCV at elevated temperatures (Chapter V)*

Before proceeding to the degradation mechanism under an electrolysis current, the degradation of LSCF electrodes under OCV must be understood first. Thus, this part of work investigates the degradation phenomenon and mechanism of LSCF electrodes kept in a high-temperature test station but without electrolysis current. The electrochemical behaviours of LSCF electrodes during anneal were obtained under various testing conditions. Surface compositional changes of the LSCF particles in the electrode along with the tests were tested.

- *Investigation of the electrochemical behaviours of LSCF electrodes under electrolysis current (Chapter VI)*

After the study on the degradation mechanism of LSCF electrodes under OCV, the effect of the electrolysis current on the behaviours of LSCF electrodes is inspected in this part. LSCF electrodes sintered at different temperatures were firstly applied with electrolysis current of 0.2 A cm^{-2} to

study the effect of sintering temperature. After that, effect of gradually increasing electrolysis current and alternate applied electrolysis current on the electrochemical behaviours of LSCF electrodes was also investigated.

- *Investigation of the activation and delamination of LSCF electrodes under electrolysis current (Chapter VII)*

Under high electrolysis current of 1 A cm^{-2} , the LSCF electrode sintered at 1000°C on YSZ electrolytes delaminated after being tested for 24 h at 800°C . Before the delamination, there was an obvious activation process, in agreement with the above test with a current density of 0.2 A cm^{-2} . The underlying physics of the activation–delamination behaviour were studied. It was found that the formation of SrZrO_3 during the fabrication stage and the diffusion of Co during the SOEC operation were the cause for the delamination phenomenon.

- *Short-term stability test on half-cells with dense GDC interlayer and with other different configurations (Chapter VIII)*

In this chapter, short-term electrolysis tests under high electrolysis current of 1 A cm^{-2} at 800°C for extended duration, up to 264 h, were conducted on half-cells with 6 different configurations. In light of above study, prevention of the formation of SrZrO_3 second phase is critical to tackle the delamination problem. The effectiveness of sintering LSCF electrodes at 800°C and the use of a dense GDC interlayer, which can prevent the formation of SrZrO_3 second phase, in preventing the delamination problem can be examined by the short-term test. In addition, by comparing the performance of half-cells with different configurations, the effect of the air electrode–electrolyte interface on the short-

term stability of LSCF electrodes can be better understood. At the end, the most durable cell will be identified as a baseline cell for future test and improvement.

Chapter II Literature Review

2.1 Fundamentals of SOECs

RSOC is an energy conversion device which can either work as an SOFC to convert the chemical energy in hydrogen into electricity and heat or work as an SOEC to convert the electricity and heat into the chemical energy in hydrogen. In the following sections, the cell structure, working principle, general performance and efficiency analysis of an SOEC are introduced.

In this review, only the SOEC with anionic conductive electrolytes (O^{2-} -SOEC) is included. Another type of SOEC employs protonic conductive electrolytes (H^+ -SOEC) and the reactions happening on the electrodes are slightly different from the O^{2-} -SOEC. The conductivity of protonic conductive electrolytes is usually 1 magnitude higher than that of anionic conductive electrolytes (Kreuer, 2003; Medvedev et al., 2016). Hence, it is considered as a promising electrolyte materials for low-temperature and high-performance application. However, the research on H^+ conductive electrolyte is in its infant stage and this kind of electrolytes still suffer from poor mechanical property, difficulties in fabrication and poor chemical stability. Thus, more work needs to be conducted on the electrolytes of H^+ -SOEC before proceeding to the investigation on the electrode materials. As this study focuses on the stability of air electrodes, O^{2-} -SOEC was used and H^+ -SOEC will not be discussed. Also, SOEC refers to O^{2-} -SOEC exclusively for the whole dissertation.

2.1.1 Cell Structure and Working Principle

As shown in Figure II-1, a unit SOEC is composed of a gas-tight electrolyte sandwiched by two porous electrodes, anode and cathode. With the aid of electricity, the water supplied to the cathode is reduced to hydrogen and oxygen ions are released through the following reaction:

Subsequently, the oxygen ions are transferred through the electrolyte to the anode, where they are oxidized to oxygen molecules:

Combining Eq. II-1 and Eq. II-2, the overall cell reaction is:

Generally, the above mentioned reactions take place at triple phase boundary (TPB) sites, where ionic conductor (electrolyte), electronic or mixed conductor (electrode) and gas phase meet.

In the fuel cell mode, hydrogen is supplied to the anode of an SOFC and oxidized by the oxygen ions transferred from the cathode forming water and generating electrons:

The electrons are conducted through an external circuit to the cathode where oxygen molecules are reduced to oxygen ions:

Thus, the overall reaction is:

It should be noted that the anode of SOFC and the cathode of SOEC are actually the same side of the cell, i.e., the materials used in the electrode is the same one. Therefore, to avoid ambiguity, the electrode where water reduction reaction or hydrogen oxidation reaction takes place is referred to as fuel electrode and the electrode where oxygen evolution reaction or oxygen reduction reaction takes place is referred to as air electrode.

Figure II-1 Schematic diagram of a unit (a) solid oxide electrolyzer cell and (b) solid oxide fuel cell.

Additionally, during the practical operation of RSOC, air electrode is usually supplied with ambient air. As for fuel electrode, in SOFC, hydrogen containing 3% water vapour is provided for better performance, while in SOEC, water vapour is usually fed together with a certain amount of hydrogen, to prevent the oxidation of Ni particles, which is widely employed as the catalyst in fuel electrodes.

2.1.2 Materials for SOECs

The selection of materials for SOECs should consider a variety of factors such as functionality, compatibility for each component used in SOECs, namely

the electrolyte, cathode, anode, interconnect, seal, etc.. As for functionality, the parameters that should be considered are conductivity, catalytic properties, sintering temperatures as well as materials stability at operating temperatures. The compatibility factor includes the compatibility between the different materials used, for instance, thermal expansion coefficient, which is essential to ensure a longer lifespan and stability at elevated temperatures. In addition, cost effectiveness is also a limiting factor for selecting materials for SOEC systems in large-scale industrial application (Meng Ni et al., 2008).

The research and development of SOECs have been promoted since the 1960's and various materials have been found suitable for the different components in SOECs. In the following sections, the commonly used materials for air electrodes, fuel electrodes, and electrolytes are summarized. Materials for the interconnect, seal and other components employed in the fuel cell stack and system are excluded, since this work focuses on the single cell level.

2.1.2.1 Electrolyte Materials

The primary function of an electrolyte in SOECs is to conduct oxygen ions from the fuel electrode to the air electrode during operation. The electrolyte also serves as a separator to prevent the mixing of the fuel and oxidant. Hence, an ideal electrolyte should be stable in both reducing and oxidizing environments at high temperatures, impermeable to the reaction gases and possess sufficient ionic conductivity at the desired operating temperatures. Several key requirements are listed as follows:

- High ionic conductivity and negligible electronic conductivity.
- Chemical, phase, morphological and dimensional stability under processing and operating conditions.

- No detrimental chemical interaction or inter-diffusion with adjacent components.
- No gas permeability.
- Matching thermal properties with adjacent components.

A few examples of existing electrolyte materials are yttria-stabilized zirconia (YSZ), Scandia stabilized zirconia (SSZ), gadolinia doped ceria (GDC), samarium doped ceria (SDC), and lanthanum strontium gallate magnesite (LSGM) (Ishihara et al., 1994; Minh, 1993; Shemilt et al., 2000; Steele, 2000; Van herle et al., 1996). Each type of electrolyte has its own advantages and disadvantages which are summarized in Table II-1.

Table II-1 Advantages and disadvantages of different electrolytes in SOECs

Electrolyte	Advantages	Disadvantages
YSZ	<ul style="list-style-type: none"> • Excellent stability in oxidizing and reducing environment; • Excellent mechanical stability; • Good long-term stability. 	<ul style="list-style-type: none"> • Relatively low ionic conductivity; • Reaction with certain cathode materials (e.g. LSCF).
ScSZ	<ul style="list-style-type: none"> • High ionic conductivity; • Excellent stability in oxidizing and reducing environment; • Excellent mechanical stability; • Good long-term stability. 	<ul style="list-style-type: none"> • High cost; • Reaction with certain cathode materials (e.g. LSCF).
GDC/SDC	<ul style="list-style-type: none"> • High ionic conductivity; • Compatible with cathode materials. 	<ul style="list-style-type: none"> • Electronic conduction at high temperature and low O₂ partial pressures → Electronic leakage;
LSGM	<ul style="list-style-type: none"> • High ionic conductivity; • Compatible with cathode materials. 	<ul style="list-style-type: none"> • Ga evaporation at low O₂ partial pressures; • Incompatible with NiO; • Low mechanical stability; • High cost of Ga.

2.1.2.2 Fuel electrode Materials

Depending on the cell configuration, the main function of the SOEC fuel electrode is to provide support for the cell as well as reaction sites for the electro-chemical reduction of the fuel. Hence, ideal fuel electrode materials should possess the following characteristics:

- High electronic and ionic conductivity to minimize ohmic loss.
- Good catalytic activity for fuel reduction.
- Chemical, phase, morphological and dimensional stability under high temperature reducing environment.
- No detrimental chemical interaction or inter-diffusion with adjacent components at elevated temperatures.
- Sufficient porosity that allows the reactants to diffuse to the reaction sites inside the cathode as well as the products to diffuse away from the reaction sites.
- Matching thermal properties with adjacent components from room temperature to operating and fabricating temperatures to avoid cracking and delamination.

Usually, the fuel electrode is composed of metal cermet like Ni–YSZ or Ni–GDC. Recently, novel perovskite fuel electrodes are also under investigation for improved stability and tolerance to the impurities in the fuel. Table II-2 summarizes the electrochemical performance of some commonly used fuel electrode.

Table II-2 Fuel electrode materials and respective polarization resistance in the form of symmetrical cells or half-cells

Air electrode	Electro-lyte	feedstock	T (°C)	R_p ($\Omega \text{ cm}^2$)	Ref.
Ni–YSZ	YSZ	3% H ₂ O– 97% H ₂	700	0.5	(Dasari et al., 2013)
			750	0.9	
			800	1.6	
			850	2.8	
	YSZ	70% H ₂ O– 30% H ₂	800	0.098	(C. K. Lim et al., 2017)
Ni–GDC	Reports for half-cell tests are not available.				
La _{0.75} Sr _{0.25} Cr _{0.5} Mn _{0.5} O _{3-δ}	LSGM	50% H ₂ O– 50% H ₂	700	0.34	(Xing et al., 2015)
			750	0.57	
			800	0.94	
			850	1.30	
La _{0.3} Sr _{0.7} TiO _{3-δ} –SDC (65:35)	YSZ	50% H ₂ O– 50% H ₂	800	~6.5	(J. Zhang et al., 2014)
(La _{0.3} Sr _{0.7}) _{0.9} Ti _{0.9} Ni _{0.1} O _{3-δ} –SDC (65:35)	YSZ	50% H ₂ O– 50% H ₂	800	~4.5	(J. Zhang et al., 2014)

2.1.2.3 Air Electrode Materials

The primary function of the air electrode is to provide reaction sites for the electrochemical oxidation of oxygen ions into oxygen molecules during electrolyzer cell mode. Hence, ideal materials should possess the following characteristics:

- High electronic and ionic conductivity to minimize ohmic loss.
- Good catalytic activity for the oxidation of oxygen ions.
- Chemical, phase, morphological and dimensional stability under high temperature oxidizing environment.
- No detrimental chemical interaction or inter-diffusion with adjacent components at elevated temperatures.
- Sufficient porosity that allows the generated oxygen to diffuse away from the reaction sites inside the electrode.
- Matching thermal properties with adjacent components from room temperature to operating and fabricating temperatures to avoid cracking and delamination.

In addition to these characteristics, other desirable properties of an SOEC air electrode are high strength and toughness, ease of fabrication and low cost. Only noble metals and oxides with mixed ionic and electronic conductivity can be used as air electrodes in SOECs due to the high operating temperature. However, noble metals such as platinum and palladium are not cost effective and therefore not suitable for practical and large-scale applications. Perovskite oxides with the arrangement ABO_3 possess reasonable electronic and ionic conductivity at high temperatures and can therefore be considered as an SOEC air electrode. The most common air electrode materials are lanthanum strontium manganite (LSM), lanthanum strontium cobalt oxide (LSC), lanthanum strontium cobalt ferrite (LSCF), and barium strontium cobalt ferrite (BSCF) (Endo et al., 2000; Haile, 2004; S. P. Jiang & Love, 2003; Tai et al., 1995a, 1995b). Other air electrode materials include perovskite oxides, layered perovskite oxides, K_2NiF_4 -type structure oxides, pyrochlore oxides. Table II-3 sums the polarization resistances of different materials under OCV. Please note that some of the materials have not been tested in electrolyzer mode.

Table II-3 Air electrode materials and respective polarization resistance exposed to air in the form of symmetrical cells or half-cells under OCV

Air electrode	Electrolyte	Testing temperature (°C)	Polarization resistance ($\Omega \text{ cm}^2$)	Reference
Perovskite oxides				
La _{0.8} Sr _{0.2} MnO _{3-δ} —GDC(1:1)	YSZ	750	0.49	(S. P. Jiang, Leng, et al., 2003)
		700	1.06	
La _{0.6} Sr _{0.4} Co _{0.2} Fe _{0.8} O _{3-δ}	YSZ-SDC	700	~0.33	(S.P Jiang, 2002)
		800	~0.05	
		900	~0.012	
Brought forward.....				

Air electrode	Electrolyte	Testing temperature (°C)	Polarization resistance (Ω cm ²)	Reference
.....Carried forward				
La _{0.6} Sr _{0.4} Co _{0.2} Fe _{0.8} O _{3-δ}	GDC	502	21	(Esquirol et al., 2004)
		650	0.58	
		801	0.04	
La _{0.7} Sr _{0.3} Co _{0.7} Fe _{0.3} O _{3-δ}	YSZ	750	~4	(M. Liu et al., 1998)
		700	~8	
		650	~18	
La _{0.6} Sr _{0.4} Co _{0.2} Fe _{0.8} O _{3-δ} -GDC(1:1)	GDC	496	2.7	(W. Wang et al., 2005)
		600	0.22	
		696	0.04	
		801	0.01	
Ba _{0.5} Sr _{0.5} Co _{0.8} Fe _{0.2} O _{3-δ}	SDC	400	8.20	(Shao et al., 2004)
		470	2.15	
		532	0.59	
		586	0.20	
		678	0.03	
	YSZ	733	0.01	(Bo et al., 2008)
		750	0.66	
		800	0.27	
		850	0.077	
BaCo _{0.7} Fe _{0.2} Nb _{0.1} O _{3-δ}	SDC	500	0.94	(Zhu et al., 2009)
		600	0.13	
		700	0.02	
		800	0.01	
Ba _{0.9} Co _{0.5} Fe _{0.4} Nb _{0.1} O _{3-δ}	LSGM	600	0.45	(Z. Yang et al., 2011)
		650	0.26	
		700	0.12	
		750	0.06	
Sr ₂ Fe _{1.5} Mo _{0.5} O _{6-δ}	LSGM	900	~0.012	(Q. Liu et al., 2010)
Double perovskite oxides				
YBaCo ₂ O _{5+δ}	LSGMC*	700	0.11	(Xue et al., 2011)
		750	0.08	
		800	0.06	
SmBa _{0.75} Ca _{0.25} CoFeO _{5+δ} -GDC (3:2)	GDC	700	0.13	(Zheng et al., 2017)
		800	0.04	
Pyrochlore oxides				
Y _{1.4} Sr _{0.6} Ti ₂ O ₇	unknown	500	0.5	(Gill et al., 2011)
Bi ₂ Ru ₂ O _{7-δ}	YSZ	650	3	(Ehora et al., 2008)
K ₂ NiF ₄ -type structure oxides				
La ₂ Cu _{0.8} Co _{0.2} O ₄	GDC	750	1	(Q. Li et al., 2012)
		800	0.6	
		900	0.5	
La _{0.6} Ni _{0.4} FeO ₃	SDC	650	5.08	(X. Ding et al., 2015)
		700	1.99	
		750	0.73	
		800	0.29	

*: $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.115}\text{Co}_{0.085}\text{O}_{2.85}$

2.1.3 General Performance

The performance of an SOEC is characterized by its current–voltage relationship, or the “ I – V curve”, which shows the voltage input for a desired current of an SOEC.

The theoretical open circuit voltage (OCV, E) of an SOEC is defined by its Nernst potential. For the hydrogen–oxygen fuel cell, the Nernst equation is:

$$E = E^0 - \frac{RT}{2F} \ln \left(\frac{p_{H_2O}}{p_{H_2} \cdot p_{O_2}^{\frac{1}{2}}} \right), \quad \text{Eq. II-7}$$

where E^0 is the standard-state reversible voltage (V), R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the working temperature (K), F is the Faraday constant ($\sim 96485 \text{ C mol}^{-1}$), and p is the partial pressure. The reversible voltage under standard-state conditions is:

$$E^0 = -\frac{\Delta g_{rxn}^0}{nF}, \quad \text{Eq. II-8}$$

where Δg_{rxn}^0 is the standard-state Gibbs free energy change for the reaction. For the hydrogen–oxygen fuel cell, E^0 equals to 1.23 V under standard-state condition (1 atm, 25 °C).

During the practical operation of an SOEC, the actual cell voltage is higher than its theoretical value because of various losses. Generally speaking, there are three types of losses in total:

1. Activation losses (η_{act}) due to the electrochemical reaction at the electrode–electrolyte interface.
2. Ohmic losses (η_{ohmic}) mainly due to ionic conduction of charge carriers through the electrolyte.
3. Concentration losses (η_{conc}) due to mass transport limitation.

Considering all the losses, the actual voltage, V , of an SOEC can be expressed as:

$$V = E + \eta_{act} + \eta_{ohmic} + \eta_{conc} \quad \text{Eq. II-9}$$

A typical I - V curve of an SOEC based on Eq. II-9 is shown in Figure II-2. The three losses contribute to the characteristic shape of the SOEC I - V curve. Generally speaking, the activation losses usually dominate at low current density. However, thanks to the high operating temperature, the activation losses are very small compared with the ohmic losses and usually hard to distinguish from the ohmic losses by I - V curves. The ohmic losses control the middle current density regime. At high current density, the concentration losses are dominant.

Figure II-2 Typical I - V curve of an SOEC button cell

2.1.4 Thermodynamic Estimate of System Efficiency

In this part, thermodynamic analysis is presented for both a single SOEC and high-temperature water electrolysis system based on SOECs.

For an SOEC single cell, the total energy demanded is the enthalpy change, ΔH , described by the first law of thermodynamics as:

$$\Delta H = \Delta G + Q, \quad \text{Eq. II-10}$$

where ΔG is the Gibbs free energy or the electrical energy demand, and Q is the heat energy demand. Each term can be estimated by (Gómez & Hotza, 2016):

$$\Delta H = \Delta H^\circ + \int_{T^\circ}^T \Delta C_p dT, \quad \text{Eq. II-11}$$

$$Q = T\Delta S, \quad \text{Eq. II-12}$$

$$\Delta S = \Delta S^\circ + \int_{T^\circ}^T \frac{\Delta C_p}{T} dT, \quad \text{Eq. II-13}$$

where T is the absolute temperature, ΔC_p is the heat capacity at constant pressure, ΔS is the entropy change, ΔH° and ΔS° are, respectively, the enthalpy and entropy at the standard-state condition (1 atm, 25 °C). Thus, energy demand for hydrogen obtained by high-temperature water electrolysis can be calculated based on the data in (Mingyi et al., 2008) and shown in Figure II-3. It can be seen that the electrical energy demand is smaller than the total energy demand. Therefore, if the heat demand is satisfied by other heat sources, the electrical efficiency is possible to be higher than 100%. In addition, with the increase of operating temperature, the electrical energy demand decreases and the heat demand increases, marking a possible higher electrical efficiency.

Figure II-3 Energy demand for water electrolysis at different temperatures

Moreover, the passing of the current can generate Joule heat. When the Joule heat matches the heat demand, a thermal neutral voltage, V_{th} , has reached and no external heat is required. As a result, thermal neutral voltage is defined as (M. A. Laguna-Bercero, 2012):

$$V_{th} = \Delta H / 2F, \quad \text{Eq. II-14}$$

The V_{th} can be calculated to be 1.29 V at 800 °C based Eq. II-11 and II-14.

As for the efficiency of a high-temperature water electrolysis system based on SOECs, Pan et al. (Pan et al., 2017) has proposed a simplified system and calculated the efficiency thermodynamically with the cell performance in their experiments. Figure II-4 shows the system configuration and thermodynamic parameters at each part and Table II-4 shows the operating conditions of the system.

Firstly, liquid water is pumped from the water tank to the steam generator to generate water vapour. After that, the water vapour is transported through the

heat exchanger to preheat by the exhaust gas. The preheated water vapour is then added with hydrogen coming from the exhaust gas recycling (EGR) to have 5% hydrogen concentration to prevent the oxidation of the Ni–YSZ fuel electrode. Next, the gas mixture is sent to the SOEC cell, which is placed in a furnace to maintain the desired working temperature. The generated hydrogen is stored in high-pressure cylinder.

Figure II-4 Proposed high-temperature water electrolysis system based on 1 m² cell presented in (Pan et al., 2017) and thermodynamic parameters at each part

The area of the cell was set as 1 m² and the steam conversion rate was set as 80%. The total current, J , was 10000 A, which corresponds to a hydrogen generate rate of 0.052 mol s⁻¹ m⁻² or 4180 L h⁻¹ m⁻² according to Faraday law. According to the experiment in (Pan et al., 2017), the cell voltage was 1.13 V when the electrolysis current reached 1 A cm⁻² and they were used in the calculations on the system efficiency. Moreover, as all the hydrogen needed comes from EGR, the EGR rate was calculated to be 6.2%.

Table II-4 Designed parameters of the proposed energy storage system based on SOECs (Pan et al., 2017)

Parameter	Value
Operating temperature, T (K)	1073
Operating pressure, P (bar)	1
Operating current, J ($A\ cm^{-2}$)	1
Operating voltage, V_O (V)	1.13
Water content in inlet gas (vol %)	95
Exhaust gas recycle rate, EGR (%)	6.2
Steam conversion rate (vol %)	80
Air electrode gas	No flow
Heat loss	Negligible
Temperature of water supply ($^{\circ}C$)	25

Because the operating voltage $V_O = 1.13\ V$ is lower than the V_{th} value of $1.29\ V$, the furnace needs to provide the heat required for electrolysis, as well as the heat for the inlet gas. The SOEC was assumed to be thermally insulated without any heat loss. The heat for electrolysis Q_E is determined by (Z. Wang et al., 2010):

$$Q_E = (V_{th} - V_O) \times J. \quad \text{Eq. II-15}$$

As liquid water is fed in the system, heat is necessary to convert water into the water vapour. The heat required for water evaporation, Q_S , can be obtained by Eq. II-16 as follows:

$$Q_S = N_{H_2O} \times (H_{H_2O(g)}^{373K} - H_{H_2O(l)}^{298K}), \quad \text{Eq. II-16}$$

where N_{H_2O} ($mol\ s^{-1}$) is the flow rate of supplied water, $H_{H_2O(g)}^{373K}$ and $H_{H_2O(l)}^{298K}$ ($kJ\ mol^{-1}$) are the enthalpies of water vapour at $800\ ^{\circ}C$ and liquid water at $25\ ^{\circ}C$, respectively. The flow rate of supplied water was calculated, from the Faradic law and EGR rate, to be $0.064\ mol\ s^{-1}$. The electric consumption of the water

pump was neglected in this study as the effect is less than 0.01%. Before the water vapour is added with the EGR gas and fed to the cell, it is preheated by a heat exchanger to recover the heat from the exhaust gas. The effectiveness factor of the heat exchanger was set as 0.9.

At last, the electricity input for electrolyzing water can be obtained by simply multiplying the operating current and the applied voltage:

$$E_{\text{elec}} = V_0 \times J. \quad \text{Eq. II-17}$$

In addition, to store the generated hydrogen in high-pressure cylinder, the compression for 350-bar refuelling will consume 3 kWh kg⁻¹ of the stored hydrogen (*Energy Requirements for Hydrogen Gas Compression and Liquefaction as Related to Vehicle Storage Needs*).

At last, the system efficiency of electrolysis, η , based on the lower heating value (LHV) of hydrogen, can be obtained by Eq. II-18 as follows.

$$\eta = \text{LHV} \times N_{\text{H}_2} / W_{\text{total}}, \quad \text{Eq. II-18}$$

where W_{total} is the total input work, N_{H_2} is the flow rate of the generated hydrogen, which is 0.052 mol s⁻¹. LHV of hydrogen is 120.21 MJ kg⁻¹.

Figure II-5 shows the electric power consumed by water electrolysis process, the steam generator, the SOEC furnace and the hydrogen storage in high-pressure tank (Pan et al., 2017). It can be seen that the electrolysis process consumes the most, 11.2 kW, followed by the steam generator, 3 kW. The total energy consumption is 17.1 kW while the total hydrogen generated is 12.5 kW. Thus, the overall electricity to hydrogen efficiency can be calculated to be 73% with an operating current of 1 A cm⁻², corresponding to a hydrogen generation rate of 4180 L h⁻¹ m⁻². This efficiency enables the practical deployment of such

a high-temperature water electrolysis system as a way to store the excess renewable energy.

Figure II-5 Electric power consumed by water electrolysis process, the steam generator, the SOEC furnace and the hydrogen storage in high-pressure tank (Pan et al., 2017)

2.2 Recent Development of SOECs

2.2.1 State-of-the-art Materials and Performance

In Table II-5, performances of the full cells that have been presented for pure water electrolysis in the literature till now are presented. Materials for air electrodes, fuel electrodes and electrolytes are listed. Feedstock used is also indicated as it can affect the performance significantly in SOEC. The performances are demonstrated by the applied voltage when the electrolysis current reaches 0.5 A cm^{-2} .

Table II-5¹ Voltages of full cells measured at 800 °C for pure water electrolysis at 0.5 A cm⁻²

Air electrode	Hydrogen electrode	Electrolyte (Thickness/ μm)	Feedstock (H ₂ O-H ₂ -balance gas)	Voltage (V)	Reference
BSCF	Ni-YSZ	YSZ-SDC (4–18)	70%–30%	1.21	(Heidari et al., 2017)
BSCF	Ni-YSZ	YSZ-SDC (30–10)	70%–30%	1.35	(P. Kim-Lohsoontorn et al., 2010)
LSCF1982	Ni-YSZ	YSZ-GDC (8–2)	~92%–8%	1.06	(Choi et al., 2013)
LSCF1982-GDC (1:1)	Ni-YSZ	YSZ-GDC (8–2)	~92%–8%	1.20	(Choi et al., 2013)
LSCF6428 impregnated YSZ	Ni-YSZ	YSZ (22.5)	50%–25%–25% Ar	1.08	(Fan, Keane, Li, et al., 2014)
LSCF-GDC (3:2)	Ni-YSZ	Zr _{0.9} Sc _{0.1} O _{1.95} -GDC (2.6–2)	80%–20%	0.96	(Mahmood et al., 2015)
SrCo _{0.8} Fe _{0.1} Ga _{0.1} O _{3-δ}	Ni-YSZ	YSZ-Ce _{0.2} Gd _{0.8} O _{1.9} (11–3)	40%–60%	1.14	(Meng et al., 2016)
² Nd ₂ O ₃ -Nd ₂ NiO _{4+δ} impregnated SSZ	Ni-SDC impregnated 430 L-YSZ	Zr _{0.88} Sc _{0.22} Ce _{0.01} O _{2.12} (15)	50%–50%	1.05	(T. Chen et al., 2015)
(La _{0.8} Sr _{0.2}) _{0.98} MnO _{3-δ} -YSZ (unknown ratio)	Ni-YSZ	YSZ (10)	50%–50%	1.13	(Sun et al., 2015)
YSZ impregnated LSM	Ni-YSZ	YSZ (33)	70%–30%	1.16	(C. Yang et al., 2010)
La _{0.8} Sr _{0.2} MnO _{3-δ} -YSZ (1:1)	Ni-YSZ	YSZ (unknown)	70%–30%	1.42	(Pattaraporn Kim-Lohsoontorn et al., 2011)
³ (La _{0.75} Sr _{0.25}) _{0.95} MnO ₃ -YSZ (3:2)	Ni-YSZ	YSZ (13)	60%–40%	1.47	(Liang et al., 2009)
Nd ₂ NiO _{4+δ}	Ni-GDC	3% Y ₂ O ₃ -ZrO ₂ (90)	90%–10%	1.20	(Chauveau et al., 2010)
Carried forward.....					

Oxygen electrode	Hydrogen electrode	Electrolyte (Thickness/ μm)	Feedstock (H ₂ O-H ₂ -balance gas)	Voltage (V)	Reference
.....Brought forward					
Ba _{0.9} Co _{0.5} Fe _{0.4} Nb _{0.1} O _{3-δ}	Ni-GDC	LSGM (250)	60%–40%	1.08	(Z. Yang et al., 2011)
⁴ LSCF6482	LSCM	LSGM (250)	50%–50%	1.43	(Xing et al., 2015)
⁵ LSCF6482	LSCM-Cu	LSGM (250)	50%–50%	1.28	(Xing et al., 2015)

1. In the table, YSZ denotes 8% Y₂O₃–ZrO₂; GDC denotes Ce_{0.1}Gd_{0.9}O_{1.95} unless noted otherwise; SDC denotes Sm_{0.2}Ce_{0.8}O_{1.9}; BSCF denotes Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3- δ} ; LSCF6428 denotes La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3- δ} ; LSCF1982 denotes La_{0.1}Sr_{0.9}Co_{0.8}Fe_{0.2}O_{3- δ} ; LSCF6482 denotes La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3- δ} ; LSCM denotes La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.4}O_{3- δ} ; LSGM denotes La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17}O_{3- δ}

2. The cell is a 430L stainless steel-supported cell.

3. The cell was tested at 850 °C

4. The voltage of the cell was obtained at 0.2 A cm⁻²

5. The cell was tested at 750 °C

2.2.2 Degradation of SOECs

Till now, several durability studies on full cells operated as SOEC have been conducted (Schefold et al., 2015a; Schiller et al., 2008; Tietz et al., 2013). In 2008, Deutsches Zentrum für Luft- und Raumfahrt (DLR) has conducted an aging study for more than 2000 h on a metal supported Ni-YSZ|YSZ|LSCF cell (Schiller et al., 2008). The cell showed an average voltage increase of 72 mV kh^{-1} at 800 °C under electrolysis current density of 0.3 A cm^{-2} . After that in 2013, Tietz et al. (Tietz et al., 2013) performed an aging test on Ni-YSZ|YSZ|GDC|LSCF fuel electrode-supported cell for more than 9000 h at 778 °C under an electrolysis current of 1 A cm^{-2} . A voltage increase of 40 mV kh^{-1} was observed. In the above two tests, the electrolytes used were all thin-film electrolyte. Recently in 2015, Schefold et al. (Schefold et al., 2015a) conducted an electrolysis test for over 11,000 h on an electrolyte-supported cell for the first time. The average voltage increase was only 7.3 mV kh^{-1} for the Ni-GDC|GDC|6Sc1CeSZ|GDC|LSCF cell tested at around 848 °C under electrolysis current density of 0.9 A cm^{-2} . This result is the most encouraging one so far, it is smaller than the 10.6 mV kh^{-1} voltage loss of an SOFC tested for 9,630 h in a five cell stack composed of Ni-YSZ|YSZ|GDC|LSCF fuel electrode-supported cells (Comminges et al., 2012), showing that the practical implementation of SOECs is viable.

In Table II-6, the degradation mechanisms recognized in the previous studies have been summarized and the testing conditions are indicated together. There are two things that need to be pointed out. Firstly, after the short- or long-term tests, although several changes on the cell have been spotted, it is hard or even impossible to recognize the main cause of the degradation. In another word, how a spotted change can affect the electrochemical performance is not clear. Secondly, studies on the solutions to the degradation of SOEC are limited. More efforts should be spent on dealing with the degradation.

Table II-6 Degradation mechanisms of SOECs

Component	Materials	Mechanism	Operating Condition	Reference
Fuel electrode	Ni–YSZ	Surface roughness of the Ni particles	• Full cell under electrolysis current of 1 A cm ⁻² at 778 °C for 9000 h	(Tietz et al., 2013)
		Increase of Ni particle size	• Full cell under electrolysis current of 0.5 A cm ⁻² at 850 °C	(Hauch et al., 2008)
		Relocation of Ni particle and formation of dense Ni–YSZ layer at the electrode–electrolyte interface	• Full cell under electrolysis current of 2 A cm ⁻² at 850 °C	(Hauch et al., 2008)
		Si-containing impurities	• Full cell under electrolysis current of 0.5 A cm ⁻² at 850 °C	(Hauch et al., 2008)
		Si-containing impurities in the inlet	• Full cell under electrolysis current of 2 A cm ⁻² at 850 °C for ~200 h	(Knibbe, Traulsen, et al., 2010)
Electrolyte	YSZ	Grain boundary fracture (Intergranular cracks)	• Full cell under electrolysis current of 2 A cm ⁻² at 850 °C for ~200 h • Symmetric cell under electrolysis current of 1.5 A cm ⁻² at 750 °C for 120 h	(Knibbe, Traulsen, et al., 2010) (J. Kim et al., 2013)
		Increased porosities	• Full cell under electrolysis current of 2 A cm ⁻² at 850 °C for ~200 h	(Knibbe, Traulsen, et al., 2010)
	YSZ–GDC	Formation of a dense layer at the YSZ–GDC interface composed of YSZ, GDC and SrZrO ₃	• Full cell under electrolysis current of 1 A cm ⁻² at 778 °C for 9000 h	(Tietz et al., 2013)
Carried forward.....				

Component	Materials	Mechanism	Operating Condition	Reference
.....Brought forward				
Electrolyte	YSZ–GDC	Delamination of GDC interlayer	<ul style="list-style-type: none"> Full cell under electrolysis current of 1.5 A cm⁻² at 800 °C for ~300 h Full cell under electrolysis current of 0.3 A cm⁻² at 850 °C Full cell under electrolysis current of 0.8 A cm⁻² at 800 °C for 100 h 	(Hjalmarsson et al., 2013) (Fan, Keane, Singh, et al., 2014) (Kim & Choi, 2014)
Air electrode	LSM–YSZ	Delamination	<ul style="list-style-type: none"> Modelling Half-cell under electrolysis current of 0.5 A cm⁻² at 800 °C for 48 h Full cell I–V curve test until electrolysis current of 2.75 A cm⁻² Symmetric cell under voltage of 0.8 V at 840 °C for 100 h Symmetric cell under electrolysis current of 1.5 A cm⁻² at 750 °C for 120 h 	(Anil V. Virkar, 2010) (K. Chen et al., 2011) (M. Laguna-Bercero et al., 2011) (Keane et al., 2012) (J. Kim et al., 2013)
		Formation of small grains in the YSZ grains	<ul style="list-style-type: none"> Full cell under electrolysis current of 2 A cm⁻² at 850 °C for ~200 h 	(Knibbe, Traulsen, et al., 2010)
		Delamination	<ul style="list-style-type: none"> Full cell under electrolysis voltage of 1.3 V at 800 °C for 50 h 	(Kim & Choi, 2013)
		Compositional fluctuations and re-crystallization	<ul style="list-style-type: none"> Full cell under electrolysis current of 1 A cm⁻² at 778 °C for 9000 h 	(Tietz et al., 2013)
	LSCM–YbScSZ*	Delamination	<ul style="list-style-type: none"> Symmetric cell under electrolysis current of 0.3 A cm⁻² at 850 °C for 7 h 	(Torrell et al., 2015)

*: YbScSZ, Yb_{0.06}Sc_{0.04}Zr_{0.9}O_{1.95}

2.3 Degradation of Air Electrodes

2.3.1 Delamination of Air Electrodes

2.3.1.1 Delamination of LSM-Based Air Electrodes

Several groups have tried to identify the delamination mechanism of LSM-based electrodes during the electrolysis test both experimentally and computationally.

Experimentally, Chen et al. (K. Chen et al., 2012a; K. Chen & Jiang, 2011) have conducted experiments with electrolysis current of 0.5 A cm^{-2} at 800°C on a pure LSM air electrode for 48 h or on an LSM–YSZ composite air electrode for 80 h. They have observed formation of nanoparticles in the range of 50–100 nm, which can be removed by HCl acid treatment, on the surface of the YSZ electrolytes after the delamination. They proposed that the disintegration of LSM bulk particles into nanoparticles was the origin of delamination. Firstly, oxygen ion migrated into LSM lattice, leading to the increase of the oxidation state of Mn from mixed of $3^+–4^+$ to 4^+ (Backhaus-Ricoult et al., 2008; W Wang et al., 2004), giving rise to a localized tensile strain. This tensile strain favoured the formation of oxygen vacancies within LSM and the accumulation of oxygen vacancies would eventually lead to the formation of micro-cracks and individual nanoparticles. Gradually, the propagation of micro-cracks and continuous formation of individual nanoparticles resulted in the delamination of LSM electrode. Later, Zhang et al. (Yanxiang Zhang et al., 2012) have proposed a model based on the theory above, which can accurately predict the evolution of the R_p during the delamination.

Keane et al. (Keane et al., 2012) argued that the delamination of LSM air electrode is caused by the formation of second phase, $\text{La}_2\text{Zr}_2\text{O}_7$. They

concluded that the formation of $\text{La}_2\text{Zr}_2\text{O}_7$ is more favourable in electrolyzer mode based on the facts that formation at the air electrode–electrolyte interface was attributed to the oxidative reactions shown in Eq. II-19 and Eq. II-20 (strontium is excluded for simplicity) (Labrincha et al., 1993) and the Gibbs free energy of the second reaction becomes negative at oxygen partial pressure above approximately 3.7 atm (M. Chen, 2005). In the meantime, they calculated that the air electrode–electrolyte interface oxygen partial pressure can reach 10^{13} atm at 0.8 V and 10^4 atm maximally at 0.3 V according to the equations in Reference (Anil V Virkar et al., 1990). This formation of second phase would further induce the formation of pores at the grain boundary of YSZ electrolytes and weaken the interface of electrolyte and air electrode. Eventually, the delamination of air electrode occurred.

Modelling work done by Virkar (Anil V. Virkar, 2010) showed that high oxygen partial pressure could develop within the electrolyte near the electrolyte–air electrode interface, causing the delamination of electrode. His model also pointed out that the higher the electronic conductivity of the electrolyte, the lower is the tendency for the formation of high internal pressures. Laguna-Bercero and co-workers (M. Laguna-Bercero et al., 2011) tested a cathode-supported Ni–YSZ|YSZ|LSM–YSZ cell under extreme high voltage up to 2.8 V and found high oxygen partial pressure gradient taking place at the electrolyte–air electrode interface, supporting the above model.

Rashkeev and Glazoff (Rashkeev et al., 2012) used a combination of first-principles, density-functional-theory (DFT) calculations and thermodynamic modelling to elucidate the main processes that contribute into the delamination

of air electrode consisting of LSM–YSZ composite air electrodes. They found that the inter-diffusion of different atoms across the LSM–YSZ interface significantly affected structural stability of the materials and their interface. Particularly, La and Sr substitutional defects positioned in ZrO_2 oxide and near LSM–YSZ interface significantly changed oxygen transport which might develop pressure build-up in the interfacial region and eventually develop delamination process.

Kim et al. (J. Kim et al., 2013) have applied electrolysis current of 1.5 A cm^{-2} at 750°C for 120 h on symmetric cells composed of YSZ electrolytes and LSM–YSZ electrodes. After the test, extensive inter-diffusion between the two phases and intergranular fracture along YSZ grain boundaries were observed. They discussed that the migrated La, Sr and Mn impurities would segregate along the grain boundary of YSZ electrolyte and participate in structural degradation by facilitating generation of oxygen gas. This experiment supports above modelling work done by Rashkeev and Glazoff (Rashkeev & Glazoff, 2012). Therefore, it is critical to suppress the cation migration to improve the long-term stability in SOEC operating conditions, especially under high polarization with large external electric field and high oxygen flux.

2.3.1.2 Delamination of LSCF-Based Air Electrodes

Kim and Choi (Kim & Choi, 2013) have reported the delamination of LSCF electrodes after testing at 800°C with an applied voltage of 1.3 V for 50 h on a Ni–YSZ|YSZ|GDC|LSCF fuel electrode-supported full cell. Even though gadolinium doped ceria (GDC) was employed as an interlayer, the delamination of the GDC interlayer from the YSZ electrolyte has also been observed (Fan, Keane, Singh, et al., 2014; Hjalmarsson et al., 2013; Kim & Choi, 2014). However, till now the delamination mechanism of LSCF electrodes is still

unclear. Thus, it is urgent to understand the mechanism in order to improve the stability.

2.3.1.3 Possible Solutions for the Delamination

Chen et al. (K. Chen et al., 2012b) characterized the stability of an LSM infiltrated YSZ air electrode under electrolysis current of 0.5 A cm^{-2} for 100 h at 800°C . They found that the microstructural stability of LSM nanoparticles was governed by two opposite effects; the grain growth by the thermal sintering effect and the LSM lattice shrinkage under the anodic polarization as mentioned above (K. Chen & Jiang, 2011). Thus, for the LSM infiltrated YSZ air electrode sintered at 900°C , the performance evolution was governed by the thermal sintering effect which results in particle size increase and performance degradation. In contrast, for the air electrode sintered at 1100°C , the performance evolution was dominated by the LSM lattice shrinkage, leading to particle sized decrease and performance activation. Consequently, the long-term stability of nano-structured LSM–YSZ composite oxygen electrodes could be manipulated by controlling and optimizing of the infiltrated LSM nanoparticles.

Li et al. (N. Li et al., 2013) applied Mn modification on the YSZ electrolyte, in order to reduce the formation of $\text{La}_2\text{Zr}_2\text{O}_7$, which is the cause of delamination according to the study by Keane et al. (Keane et al., 2012). After electrolysis test with a voltage bias of 0.8 V for 200 h at 840°C , no delamination was found after the test. In addition, the Mn-doped cell showed slower $\text{La}_2\text{Zr}_2\text{O}_7$ formation and corresponding smaller ohmic and non-ohmic resistance change compared to the un-doped cells. It was also hypothesized that the porous sol-gel coating of Mn prevents high pressure oxygen build-up and results in the mitigation of the anode delamination.

In light of the modelling work done by Virkar (Anil V. Virkar, 2010), Lim and his co-workers (H.-T. Lim et al., 2009; Park et al., 2014) increased the electronic conductivity of the electrolyte and studied its effectiveness in mitigating the delamination problem. At the beginning, Lim and Virkar (H.-T. Lim & Virkar, 2009) doped 8% CeO₂ into the YSZ electrolyte of a Ni-YSZ|YSZ|LSM-YSZ. After three consecutive electrolysis DC bias, 0.31 V (Relative to OCV in electrolyzer mode) for 170 min, 0.67 V for 90 min and 0.57 V for 270 min, the cell with Ce doped YSZ showed no delamination while the air electrode on un-doped YSZ has fully delaminated with an increase of ohmic resistance from 0.3 to 0.8 $\Omega \text{ cm}^2$. However, this method could lead to current leakage which would in turn lower the efficiency. Later, Park et al. (Park et al., 2014) have fabricated a bilayer electrolyte composed of CeO₂ doped YSZ and pure YSZ. The OCV of the Ni-YSZ|YSZ|CeO₂ doped YSZ|LSM-YSZ full cell was close to theoretical value. After tested under electrolysis bias of 0.23 V for 250 min, the cell structure remained intact without sign of delamination, indicating that the bilayer electrolyte could effectively alleviate the problem.

To deal with the delamination of GDC interlayer when it was used to prevent the reaction between LSCF and YSZ, Kim et al. (Kim et al., 2015) has added an Ce_{0.43}Zr_{0.43}Gd_{0.1}Y_{0.04}O_{2- δ} contact layer between the YSZ electrolyte and the GDC interlayer. *I-V* curve obtained at 800 °C with a feedstock of 80% H₂O–20% H₂ revealed that the addition of this contact layer could decrease the voltage from 1.30 V to 1.24 V at electrolysis current density of 1 A cm⁻². The authors discussed that the improvement of performance was a result of the higher ionic conductivity of the contact layer than the inter-diffusion layer between YSZ and GDC when a contact layer was not used. Electrolysis test at

800 °C under an electrolysis current of 0.8 A cm⁻² for 100 h with a feedstock of 80% H₂O–20% H₂ was conducted on cells with and without contact layer. After the test, GDC interlayer delamination was observed on the cell without Ce_{0.43}Zr_{0.43}Gd_{0.1}Y_{0.04}O_{2-δ} contact layer. They concluded that the contact layer could also improve the stability of the electrolyte.

In addition to the above improvement on stability by modification on the cell structure, a few groups (Graves et al., 2015; Hughes et al., 2013; Rashkeev et al., 2011) have also reported that the stability can be improved by optimizing the operating strategy.

Modelling work done by Rashkeev and Glazoff (Rashkeev & Glazoff, 2011) indicates that applying AC voltage pulses at a certain frequency range to SOECs could reduce oxygen delamination degradation in these devices and significantly increase their lifetime without any significant modification of SOEC materials and design.

Hughes et al. (Hughes et al., 2013) have tested LSM–YSZ symmetric cells at 800 °C in air with current densities of 0.5 and 1.5 A cm⁻², with current cycle periods of 1 and 12 h. Firstly, they found that cells tested at a reversing current of 0.5 A cm⁻² showed no measurable resistance increase while cells tested at a reversing current of 1.5 A cm⁻² presented continuous increase in resistances. Further, with a reversing current of 1.5 A cm⁻², the cell with a cycle period of 12 h showed more severe degradation than that with a cycle period of 1 h. Nonetheless, all the cells were more stable compared with the cell with continuous electrolysis test under 1.5 A cm⁻². Since the existing mechanisms for delamination involve formation of a new phase or a void and have an incubation time, the authors believed that the suppression of degradation by rapidly switching current direction was reasonable.

On a Ni-YSZ|YSZ|LSM-YSZ full cell, Graves et al. (Graves et al., 2015) have initially applied cycles with electrolyzer mode under 1 A cm^{-2} for 1 h and fuel cell mode with 0.5 A cm^{-2} for 5 h at 800°C . After testing for 420 h, the impedance of the cell operated in reversible cycling mode was nearly identical to the impedance measured before operation, showing no degradation. In contrast, the impedance of the cell operated continuously in electrolysis mode increased markedly in the frequency range of 10^1 - 10^5 Hz, and an increase in the ohmic resistance by a factor of 2.8 was observed, showing major degradation. Subsequently, the period of electrolyzer mode was extended to 2 h and further to 5 h to recognize the onset of the degradation. By increasing the electrolysis period to 5 h, the ohmic resistance gradually increased without stabilizing—albeit at a rate about 20 times slower than in constant electrolysis operation. Notably, the ohmic resistance could be returned to its original value by pausing the cycling and performing an extended 50 h operation in fuel cell mode.

Although above experiments have proposed a way to prolong the lifespan of an SOEC by adjusting the operating strategy, it should be indicated that as a device of which the purpose is to store the excess energy in the form of hydrogen, the operation condition is determined by the availability of the renewable energy. For example, the solar energy is available from 7 AM to 5 PM. Then during the 10 h where excess solar energy needs to be stored, the RSOC must operate continuously for 10 h in electrolyzer mode. At night, the RSOC needs to operate in fuel cell mode to release the energy stored in hydrogen for 14 h from 5 PM to 7 AM next day. This process repeats day by day. Once the damage is caused, it may not be recoverable. Even it is possible to return the ohmic resistance to its initial value, it is not practical to operate it in fuel cell

mode for prolonged duration. Consequently, optimization on the cell materials and structure is still critical in achieving practical SOEC lifespan.

2.3.2 Degradation of LSCF-based Air Electrodes

Till now the degradation of LSCF-based electrodes during electrolysis has not been extensively studied. Moreover, among the limited reports, most of them were conducted on a full cell, of which the degradation comes from various components. Thus, a clear relationship between the observed changes of LSCF electrodes and the degradation of electrochemical performance cannot be built.

Tietz et al. (Tietz et al., 2013) found that after 9000 h electrolysis test, the LSCF air electrode presented both chemical and morphological changes. From the backscattered SEM image, the LSCF framework after test was not homogeneous but composed of stoichiometric fluctuations in the sub- μm range indicated by different back-scattering intensities. Accordingly, the peaks of LSCF in XRD pattern have broadened, indicating the inhomogeneity of the electrode and the existence of various perovskite compositions after the electrolysis test. Simultaneously, formation of Co_3O_4 can be detected by XRD. In addition, whereas the LSCF particles at the outer part of the electrode close to the current collector are round and tend to be individually attached to each other, the LSCF particles at the center and especially towards the electrolyte show many more crystal faces and edges. The authors explained that the perovskite minimizes the surface defects and re-crystallizes under the influence of the electrochemical gradient.

Kim and Choi (Kim & Choi, 2014) have polarized Ni-YSZ|YSZ-GDC|LSCF full cell under electrolysis current of 0.8 A cm^{-2} with a feedstock of

80% H₂O–20% H₂ at 800 °C for 100 h. They observed a phase change of LSCF electrode from rhombohedral phase to cubic phase after the test.

2.4 Electrochemical behaviour of LSCF Air Electrodes under Cathodic Current (Fuel Cell Mode)

As mentioned in above sections, the degradation mechanism of LSCF-based electrodes has not been thoroughly studied. Also, electrochemical behaviours of LSCF air electrodes during electrolysis tests were not reported. In this part, several results on the changes of LSCF electrodes upon application of cathodic current are reviewed to give some enlightenment in studying the effect of anodic current.

Baumann et al. (Baumann et al., 2005) have applied cathodic current on LSCF electrodes and found that the current can significantly activate the electrode. In their work, the LSCF electrodes were fabricated via PLD with a substrate temperature of 800 °C and thus the effect of interfacial reaction was neglected. With a cathodic bias of 1 V, the polarization resistance decreased linearly with the square root of time. In addition, they found that a repeated application of cathodic current could stabilize the performance at a certain level. With the aid of XPS, Sr concentration on the LSCF surface increased from 28 at. % to 42 at. % after cathodic treatment, while it remained at 28 at. % after anodic treatment. Thus, they have concluded that the surface concentrated Sr contributes to the activation of LSCF electrode after cathodic treatment.

Finsterbusch et al. (Finsterbusch et al., 2012) have applied different biases, from 100 to 600 mV, on LSCF|GDC|LSCF symmetrical cells for 48 h to simultaneously study the effect of cathodic bias and anodic bias on the surface properties of LSCF electrodes. The results showed that the cathodic bias did not affect the extent of Sr surface segregation. In contrast, the anodic biases were

found to inhibit Sr segregation at low voltages. The authors ascribed this phenomenon to the oxygen vacancy concentration variations.

Liu et al. (Y. Liu et al., 2014) have applied an anodic current of 200 or 500 mA cm⁻² on both pure LSCF electrodes and LSCF impregnated GDC electrodes at 750 °C for 120 h on GDC electrolytes. The behaviour of polarization resistance was complicated. For pure LSCF electrode under 200 mA cm⁻², the polarization resistance increased from 0.19 Ω cm² to 0.62 Ω cm², while under 500 mA cm⁻², the polarization resistance decreased first for 8 h from 0.87 to 0.17 Ω cm² and then increased again to 0.45 Ω cm². In case of LSCF impregnated GDC electrode, under 200 mA cm⁻², the polarization resistance decreased significantly for the first 2 h from 1.4 to 0.18 Ω cm² and finally increased to 0.34 Ω cm², which is much more stable than the pure LSCF electrode. When it comes to 500 mA cm⁻², the polarization resistance showed a fast degradation from 0.68 to 2.15 Ω cm². The authors ascribed the degradation of LSCF electrode to microstructural changes and surface compositional changes. SEM showed the agglomeration and microstructure deterioration of the LSCF and LSCF–GDC composite electrodes. On dense LSCF cathode samples, XRD and SEM results showed that cathodic current treatment resulted in the formation of SrCoOx particles on the electrode surface.

Chapter III Experimental Procedure

3.1 Sample Preparation

3.1.1 Commercial Products

Commercial products used in this work are listed in Table III-1:

Table III-1 Commercial products used in this work

Composition	Abbreviation	Source
8 mol % $\text{Y}_2\text{O}_3\text{--ZrO}_2$	YSZ	Tosoh, Japan
Butyl benzyl phthalate	BBP	Sigma-Aldrich, US
Fe_2O_3	-	Sigma-Aldrich, US
$\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_2$	GDC	Nextech, US
$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$	LSCF	Fuelcellmaterials, US
N,N-diethylaniline	DEA	Sigma-Aldrich, US
NiO	-	Sigma-Aldrich, US
Platinum paste	-	Scientific resources
Polyethylene glycol (Molecular weight = 400 g mol ⁻¹)	PEG400	Sigma-Aldrich, US
Polyvinyl butyral	PVB	Sigma-Aldrich, US
-	VEH 500	Fuelcellmaterials, US

3.1.2 Fabrication of Half-Cells

In this work, half-cells with three-electrode configuration were used (Figure III-1) to eliminate the effect of fuel electrode and focus on the performance of LSCF working electrodes.

Figure III-1 Schematic graph of an half-cell with three-electrode configuration

The procedure of the fabrication of half-cells is shown in Figure III-2. Electrolyte substrates were prepared by die pressing the powder of electrolyte material, YSZ or GDC, and firing at 1450 °C (for YSZ) or 1600 °C (for GDC) for 4 h in air, with the sintering profile shown in Figure III-3a. The electrolyte substrates are about 20 mm in diameter and about 1 mm in thickness. After that, Pt counter electrode was applied onto one side of the electrolyte in the center. Pt reference electrode was painted as a ring with a width of ~1 mm at the edge of the electrolyte on the same side of the counter electrode. The counter and reference electrodes were sintered together at 1000 °C for 2 h with a sintering profile shown in Figure III-3b.

Working electrode slurry was prepared by fully grinding the mixture of the LSCF raw powder and VEH 500 binder with a weight ratio of 1:1. The slurry was subsequently coated onto the center of the electrolyte symmetrically opposite to the counter Pt electrode by slurry coating and sintered for 2 h at the desired temperature with the sintering profile shown in Figure III-3b. The working electrode has a geometric area of 0.5 cm² with a thickness of around 15 µm. At last, another layer of Pt was applied onto the working electrode surface serving as current collector and sintered at a temperature of 50 °C less

than the sintering temperature of the working electrode for 30 min with the sintering profile shown in Figure III-3b.

Figure III-2 Flowchart for the fabrication of half-cells

Figure III-3 Sintering profiles used in this work. ((a) Sintering profile used to fabricate electrolyte substrate in half-cells; (b) Sintering profile used to fabricate other components)

In addition to half-cells with single layer electrolytes, half-cells with YSZ electrolytes and dense or porous GDC interlayers were also fabricated. The porous GDC interlayer was fabricated by spin coating GDC suspension on the YSZ electrolyte substrate and sintered at 1200 °C for 2 h. The dense GDC interlayer was prepared by wet-ceramic co-sintering method as shown in Figure III-4. At first, YSZ powder was die-pressed into pellets and pre-sintered at 900 °C with the sintering profile shown in Figure III-3b to improve the mechanical strength. Subsequently, GDC suspension was sprayed onto the YSZ substrate. After evaporation of the solvent, the YSZ–GDC bilayer electrolyte was co-sintered at 1400 °C for 4 h with the sintering profile shown in Figure III-3b. The thickness of the resulted dense GDC interlayer is around 5 μm .

For both porous and dense GDC interlayers, the GDC suspension used was the same and prepared by ball milling 1 g GDC powder, 0.5 at.% Fe_2O_3 , 0.1 g DEA, 0.1 g BBP, 0.1 g PEG400 and 0.1 g PVB in 30 g ethanol, which is listed in Table III-2. The Fe_2O_3 was added as sintering aid in order to achieve a dense GDC interlayer (Limthongkul et al., 2009; T. Zhang et al., 2001).

Figure III-4 Flowchart for the fabrication of YSZ electrolytes with dense GDC interlayer

Table III-2 Composition of GDC suspension

Component	Function	Weight (g)
GDC + 0.5 at.% Fe ₂ O ₃	Ceramic powder	1g
Ethanol	Solvent	30
N,N-diethylaniline (DEA)	Dispersant	0.1
Benzyl butyl phthalate (BPP)	Plasticizer	0.1
Polyethylene glycol 400 (PEG400)	Plasticizer	0.1
Polyvinyl butyral (PVB)	Binder	0.1

For the sake of convenience, the half-cells are referred to as “electrolyte material + (interlayer material + p (porous)/d (dense)) + air electrode material + sintering temperature” throughout this dissertation as demonstrated in

Table III-3. For example, YGdL1000 means the half-cell composed of YSZ electrolyte, dense GDC interlayer and LSCF electrode sintered at 1000 °C. Types of half-cells used will be specified in each chapter.

Table III-3 Illustration of sample codes used in this thesis

Half-cell coding rule	Example	
	Sample code	Sample description
electrolyte material + (interlayer material + p/d) + air electrode material + sintering temperature	YL800	YSZ electrolyte + LSCF electrode + Sintering at 800 °C
	YL1000	YSZ electrolyte + LSCF electrode + Sintering at 1000 °C
	GL1000	GDC electrolyte + LSCF electrode + Sintering at 1000 °C
	YGdL1000/ YGpL1000	YSZ electrolyte + Dense/porous GDC interlayer + LSCF electrode + Sintering at 1000 °C
	YPt1000	YSZ electrolyte + Pt electrode + Sintering at 1000 °C

3.1.3 Nitric Acid Treatment

3.1.3.1 Nitric Acid Etching Treatment

The aim of nitric acid etching treatment is to remove the possible surface components of LSCF particles in electrode, as the possible metal oxide precipitated on the surface is reactive with nitric acid. The step was done by soaking samples (Half-cells) into diluted nitric acid ($\text{pH} \approx 3$) for 20 min followed by washing with distilled water for three times.

3.1.3.2 Removal of LSCF Electrodes by Nitric Acid

To study the LSCF electrode–YSZ electrolyte interface, the LSCF electrode was removed and the surface of the YSZ electrolyte previously in contact with the LSCF electrode was characterized as shown in Figure III-5. The LSCF electrode was removed by soaking the half-cells in diluted nitric acid (10 wt. %) under ultrasonic for 30 min. After that, the sample was washed by distilled water and characterized by FESEM and XRD.

Figure III-5 Schematic of the characterization of LSCF electrode-YSZ electrolyte interface

3.2 Material Characterization

3.2.1 X-Ray Diffraction (XRD)

X-ray diffraction (XRD) is a unique method in determination of crystallinity of a compound. Crystals are regular arrays of atoms, and X-rays

can be considered waves of electromagnetic radiation. Atoms can scatter X-ray waves, primarily through the atoms' electrons. An X-ray striking an electron produces secondary spherical waves emanating from the electron. This phenomenon is known as elastic scattering, and the electron is known as the scatterer. A regular array of scatterers produces a regular array of spherical waves. Although these waves cancel one another out in most directions through destructive interference, they add constructively in a few specific directions, determined by Bragg's law:

$$2d\sin\theta = n\lambda. \quad \text{Eq. III-1}$$

Here d is the spacing between diffracting planes, θ is the incident angle, n is any integer, and λ is the wavelength of the beam. These specific directions appear as spots on the diffraction pattern called reflections. Thus, X-ray diffraction results from an electromagnetic wave (the X-ray) impinging on a regular array of scatterers (the repeating arrangement of atoms within the crystal), which can be used to determine the crystal phases within the compound.

X-ray diffractometer (PW1820, Philips) was adopted to check the possible reaction products between YSZ and LSCF powder mixture. Another diffractometer (Empyrean, PANalytical) was used to conduct thin film XRD characterization. X-ray scanning was conducted over a 2θ range of $20\text{--}80^\circ$ with a Cu $K_{\alpha 1}$ radiation source ($\lambda = 1.54060 \text{ \AA}$) generated at 40 mV and 40 mA.

3.2.2 Field Emission Scanning Electron Microscopy (FESEM)

A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons generated by a thermionic emitter. The electrons interact with atoms

in the sample, producing various signals that contain information about the sample's surface topography and composition. The electron beam is generally scanned in a raster scan pattern, and the beam's position is combined with the detected signal to produce an image. It usually has relative low brightness, evaporation of cathode material and thermal drift during operation. To overcome above shortcomings, a field emission scanning electron microscope (FESEM) generates the focused beam electrons by a field emission gun, also called a cold cathode field emitter.

In this work, FESEM (JSM-7600F, JEOL, Japan) was used to study the microstructures of half-cells and electrolyte surfaces. Since the samples of this work are mostly made of ceramic materials that have a poor conductivity at room temperature, the samples were coated with gold or platinum before placing into the microscope chamber for observation. In addition, with the aid of energy dispersive X-ray (EDX) detector, qualitative and semi-quantitative information on the composition of a spot, a line or an area can be obtained.

3.2.3 X-Ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive quantitative spectroscopic technique that measures the elemental composition at the parts per thousand range, empirical formula, chemical state and electronic state of the elements that exist within a material. XPS spectra are obtained by irradiating a material with a beam of X-rays while simultaneously measuring the kinetic energy and number of electrons that escape from the top 0 to 10 nm of the material being analysed.

In this work, X-ray photoelectron spectroscopy (Axis-ULTRA, Kratos) was employed to obtain the surface composition of the LSCF electrode to study the effect of high-temperature sintering and operation on its surface property.

3.3 Electrochemical Characterization

3.3.1 Electrochemical Test Station Setup

In this work, the electrochemical test was conducted on a homemade test station designed specifically for the test of RSOCs as shown in Figure III-6. The test station is composed of a potentiostat/galvanostat instrument (Autolab PG30/FRA, Eco Chimie, Netherlands), a computer, an alumina-made holder, a vertical furnace, a heating element, a boiler, two temperature controllers and a few gas tubes and flow meters. The test station is capable of testing both SOFCs and SOECs.

Figure III-6 Photos of the homemade SOC test station

3.3.1.1 Test Station Setup of Half-Cells

To focus the study on the performance of LSCF air electrodes, all the experiments were conducted on half-cells with three-electrode configuration. Figure III-7 shows a schematic of the test station setup for half-cell characterization. The half-cell was held horizontally between two 4-bore alumina rods with the working electrode facing up. To decrease the contact resistance, a Pt mesh was placed in between the sample and the rods. Within the rod, there are four small holes which allow the passage of gas and Pt wires. During the test, the working electrode was exposed to the ambient environment, and thus no sealing is required.

Figure III-7 Schematic of the test station setup for half-cells

3.3.2 Electrochemical Impedance Spectroscopy (EIS) (AC Impedance)

It is an experimental method of characterizing electrochemical systems. This technique measures the impedance of a system over a range of frequencies, and therefore the frequency response of the system, including the energy storage and dissipation properties, is revealed. AC impedance spectroscopy is used extensively in the field of solid-state ionics and electrochemistry to

separate bulk and interfacial contributions from the overall alternating-current response of a material.

Often, EIS is expressed graphically in a Bode plot or a Nyquist plot. In a Nyquist plot, the imaginary part of the impedance Z'' (capacitance) is plotted versus the real part of the impedance Z' (resistance). In this study, AC impedance spectroscopy was employed to characterize the half-cell impedances. Typical impedance spectrum and data processing methods are shown in the following sections.

3.3.3 Electrochemical Impedance Spectroscopy-Data Processing

Figure III-8 shows a typical EIS curve of a half-cell. In an EIS Nyquist plot, the impedance is composed of an inductance and a semi-arc impedance. The left intercept between the semi-arc with the x-axis represents the ohmic resistance, R_s , of the half-cell, mainly from the contribution of the electrolyte. The difference between the high- and low-frequency intercepts denotes the polarization resistance, R_p , of the working electrode. It is universally acknowledged that at the air electrode, the oxygen reduction/evolution reaction is composed of three elementary steps as schematically shown in Figure III-9, i.e. oxygen gas diffusion (gas diffusion), oxygen adsorption/desorption, dissociation/association and diffusion (mass transfer), and electron and oxygen ion transfer and incorporation of oxygen ions into electrolytes (charge transfer). Thus, the one semi-arc shown in the EIS impedance usually consists of two or more arcs with different summit frequencies and each arc represents an elementary step.

Figure III-8 Typical EIS curve of a half-cell

Figure III-9 Schematic of reaction paths of oxygen reduction/evolution on air electrodes

According to previous reports (Kammer Hansen et al., 2010; J.-W. Lee et al., 2009; A. Leonide et al., 2008; Murray et al., 2002; Schichlein et al., 2002), for a half-cell with the air electrode as working electrode, the process at the frequency higher than 10^3 Hz is related to charge transfer (electron and oxygen ion transfer) process, the process with a frequency of around 10^2 Hz represents

the mass transfer (oxygen adsorption/desorption, dissociation/association and diffusion) process and the process around 10 Hz is associated with gas diffusion. Thus, in order to identify the contribution from each process to the overall response or to resolve the change of each process during short-term tests, the following methods can be adopted.

3.3.3.1 Equivalent Circuit Fitting

An EIS curve can be fitted with one or multiple series of resistance (R)–constant phase element (CPE) unit with each unit representing an elementary step of the air electrode reaction, by a Complex Nonlinear Least Squares (CNLS) approximation. For example, Figure III-10 shows an example of the fitting result of a half-cell with LSCF sintered at 1000 °C using the parameters in Table III-4. The EIS curve was fitted with an equivalent circuit of $LR_S(CPE_H R_{P,H})(CPE_L R_{P,L})$, where L is inductance, R_S is the ohmic resistance, CPE_H and CPE_L are the constant phase elements for high- and low-frequency processes, respectively, $R_{P,H}$ and $R_{P,L}$ are the electrode polarization resistances of high- and low-frequency processes, respectively. For the constant phase element, CPE,

$$CPE = Y_0 (j\omega)^n, \quad \text{Eq. III-2}$$

where Y_0 is the admittance, j is the imaginary unit, ω is the angular frequency and n is the frequency power. For $n = 1$, CPE is a pure capacitance and for $n = 0.5$, CPE is a Warburg-type diffusion impedance (S.P Jiang, 2002). The summit frequency, f^0 , of each process can be calculated by the following equation:

$$f^0 = \frac{1}{2 \times \pi \times (R \times Y_0)^{\frac{1}{n}}} . \quad \text{Eq. III-3}$$

The summit frequencies of high- and low-frequency processes of the sample fitting are also listed in Table III-4.

In this case, generally, $R_{P,H}$ represents the charge transfer (electron and oxygen ion transfer) process, whereas $R_{P,L}$ represents the mass transfer (oxygen adsorption/desorption, dissociation/association and diffusion) process (Kammer Hansen et al., 2010; J.-W. Lee et al., 2009; Murray et al., 2002), while the gas diffusion resistance usually cannot be observed for half-cell tests with air electrodes as working electrodes are exposed to ambient air. It can be seen that the fitting results are quite reasonable from Figure III-10.

Figure III-10 Sample fitting result for the initial electrochemical response of YL1000 (Half-cells with LSCF electrodes sintered on YSZ electrolytes at 1000 °C)

Table III-4 Fitting parameters used to fit the initial electrochemical response of YL1000 (Half-cells with LSCF electrodes sintered on YSZ electrolytes at 1000 °C)

High Frequency Arc				Low Frequency Arc			
$R_{P,H}/$ $\Omega \text{ cm}^2$	$Y_{0,H}/$ $\Omega^{-1} \text{ cm}^{-2} \text{ s}^{-n}$	n_H	$f^0/$ Hz	$R_{P,L}/$ $\Omega \text{ cm}^2$	$Y_{0,L}/$ $\Omega^{-1} \text{ cm}^{-2} \text{ s}^{-n}$	n_L	$f^0/$ Hz
0.44	1.24×10^{-2}	0.60	1013	1.16	2.13×10^{-3}	0.88	144

3.3.3.2 Distribution Function of Relaxation Times (DRT)

In equivalent circuit fitting, the equivalent circuit model needs to be defined a priori without any knowledge about the real number of polarization processes contributing to the overall polarization loss of the cell. This leads very often to a severe ambiguity of the adopted model. To overcome the disadvantage, an approach for analysing impedance spectra will be used before proceeding to equivalent circuit fitting in this work, which is distribution function of relaxation times (DRT) (A. Leonide, 2010; Andre Leonide et al., 2009). This is a way to figure out how many arcs, or processes, are contained in the one arc as seen in Figure III-10. The exact calculation process of DRT curves can be found in the above references. Figure III-11 shows a sample DRT curve of the initial electrochemical response of LSCF electrode sintered at 1000 °C. It can be seen that the two peaks at 148.92 Hz and 1875.54 Hz are at the same order of magnitude of the calculated values of summit frequency shown in Table III-4 obtained by equivalent circuit fitting, indicating that the above equivalent circuit fitting is reasonable. As for the three arcs with summit frequency at 0.22 Hz, 1.81 Hz, 11.11 Hz, they are too small to be distinguished from the whole arc and fitted with reasonable parameters. Thus, they are omitted during the equivalent circuit fitting.

Figure III-11 DRT analysis of the initial electrochemical response of YL1000 (Half-cells with LSCF electrodes sintered on YSZ electrolytes at 1000 °C)

3.3.3.3 Analysis of the Difference in Impedance Spectra (ADIS)

Above methods extract information about the contributing processes from a single impedance spectrum. By contrast, analysis of the difference in impedance spectra (ADIS) (Jensen et al., 2007) uses several spectra to isolate the process contributions prior to the data treatment. This enables the identification of the contributing process to the change of the total response upon the change of the testing condition.

The method is based on the change that occurs in an impedance spectrum when an optional operation parameter such as partial pressure of a reactant, temperature, etc., is changed. An impedance spectrum is recorded just before such a change and another spectrum just after the change. The real part of the

spectra, $Z'(f)$, is differentiated with respect to $\ln(f)$, where f is the frequency.

The difference between this value obtained after the change of the testing condition, t , and the initial value at $t = 0$ is calculated and named $\Delta Z'_t(f)$, according to Eq. III-5. $\Delta Z'_t(f)$ is then plotted against f , in which fast Fourier transform (FFT) filter was used to reduce the noise.

$$\Delta Z'_t(f) = \frac{\partial(Z'_t(f))}{\partial \ln(f)} - \frac{\partial(Z'_{t=0}(f))}{\partial \ln(f)}. \quad \text{Eq. III-4}$$

An example of the use of ADIS is shown in Figure III-12. Figure III-12a is the Nyquist plot evolution during anneal at 750 °C under OCV for 24 h of the half-cell with the LSCF electrode sintered on the YSZ electrolyte at 900 °C. Figure III-12b shows the ADIS plots. It can be recognized that the process taking place at around 200 Hz changed during the test, indicating that the change comes from the change of the mass transfer process.

Figure III-12 (a) Nyquist plots of YL900 (Half-cells with LSCF electrodes sintered on YSZ electrolytes at 900 °C) for 24 h at 750 °C under OCV; (b) Analysis of the Difference in Impedance Spectra (ADIS)

3.3.4 DC Polarization Test

DC polarization technique was employed to characterize the electrolysis performance of half-cells under current loading. Current–voltage (I – V) characteristics were recorded on the cell using linear sweep voltammetry at a sweep rate of 1 mV s^{-1} .

3.3.5 Durability Test

Galvanostatic (constant current) tests were carried out to determine the stability and degradation rates of half-cells under a constant current loading. The voltage profile of the cell was recorded for a desired duration. During the test, the current was also interrupted at a desired interval to record EIS under OCV in order to learn the change of electrochemical response of the electrode along with the testing duration.

3.3.6 Sign Convention of Current Direction

To make the testing condition clear, the sign convention of current direction is defined as follows. Firstly, during durability test or EIS test under current, all the values of current density are positive and the direction of them is defined in front of it. For half-cells with air electrode as working electrode, applying anodic current or electrolysis current is indicating that the air electrode is tested under electrolyzer mode, while applying cathodic current means that the working electrode is tested under fuel cell mode. Secondly, for DC polarization test, the current density of electrolyzer mode is negative and the current density of fuel cell mode is positive.

Chapter IV Reactions between LSCF and YSZ

4.1 Introduction

It is universally acknowledged that the perovskite phase can react with YSZ forming insulating phases. In previous reports, several groups have studied the reaction products in details.

Stochiniol et al. (Stochiniol et al., 1995) have studied the chemical compatibility between $\text{La}_{y-x}\text{Sr}_x\text{MnO}_{3-\delta}$ (LSM) and YSZ. It was found that the reactions between LSM and YSZ led to the formation of $\text{La}_2\text{Zr}_2\text{O}_7$ when $x \leq 0.3$ and SrZrO_3 when $x \geq 0.3$. The x value giving the best compatibility was found to be 0.3. Combined with La deficiency, the compatibility can be improved. No reaction products could be detected for $\text{La}_{0.95-x}\text{Sr}_x\text{MnO}_{3-\delta}$ with $0.2 \leq x \leq 0.4$ after anneal for 400 h at 1470 K, and for $\text{La}_{0.65}\text{Sr}_{0.3}\text{MnO}_{3-\delta}$ even after anneal for 200 h at 1670 K.

Kindermann et al. (Kindermann et al., 1996) has conducted chemical compatibility study between $(\text{La}_{0.6}\text{Sr}_{0.4})_z\text{M}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSMF, $Z = 1, 0.9$; $M = \text{Cr, Mn, Co, Ni}$) perovskites and YSZ. After sintering at 1000 °C for 1300 h, SrZrO_3 or $\text{La}_2\text{Zr}_2\text{O}_7$ formed along with the precipitation of spinel phase, depending on the specific composition of LSMF. The experiments revealed that the trend of reactivities of the perovskites LSMF with 8YSZ followed the order $\text{Co} > \text{Ni} > \text{Cr} > \text{Mn}$. The same order of reactivity was valid for the four perovskites with sub-stoichiometry on A-site. The authors explained this order by considering the stability of SrMO_3 , as the perovskites LSMF could be

considered as solid solutions of LaMO_3 and SrMO_3 . The chemical components SrMO_3 in the perovskite phase reacted with the ZrO_2 from 8YSZ by the following reaction:

The lower was the stability of the dioxide MO_2 relative to the corresponding lower valent oxide MO_x , the more was the tendency of the dioxide MO_2 in SrMO_3 to form MO_x by the above reaction, and as a result, the higher was the reactivity of the corresponding perovskite. The observed order of reactivity thus followed the trend in stability of the tetravalent oxides relative to the lower valent oxides. In addition, they have found that the sub-stoichiometry on the A-site yielded reduced reactivity for the Cr or Mn containing perovskites while had little effect on the reactivity for the Co or Ni containing perovskites.

Kostogloudis et al. (Kostogloudis et al., 2000) also conducted studies on the compatibility between $\text{La}_{1-x}\text{Sr}_x\text{Co}_{0.2}\text{Mn}_{0.8}\text{O}_{3-\delta}$, $\text{La}_{1-x}\text{Sr}_x\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$, $\text{La}_{1-x}\text{Ca}_x\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ and YSZ by annealing equimolar powder mixtures at 1100 °C for 120 h. The reaction products were also identified to be $\text{La}_2\text{Zr}_2\text{O}_7$ and $(\text{Sr}/\text{Ca})\text{ZrO}_3$, together with the precipitation of CoFe_2O_4 .

Poulsen and van der Puil (Poulsen et al., 1992) have tested the conductivities of $\text{La}_2\text{Zr}_2\text{O}_7$ and SrZrO_3 . It was found that the conductivity of $\text{La}_2\text{Zr}_2\text{O}_7$ was $3.7 \times 10^{-6} \text{ S cm}^{-1}$ and of SrZrO_3 is $4.3 \times 10^{-6} \text{ S cm}^{-1}$ at 750 °C. Generally, the conductivity of LSCF is at the magnitude of 10^2 S cm^{-1} . The low conductivities of these insulting phases generated from interfacial reactions can

affect both the transference of oxygen ions and electrons, and thus lower the electrochemical performance. Fu et al. (Fu et al., 2008) have sintered $\text{La}_{0.58}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ at different temperatures on YSZ electrolytes in half-cells. They found that with the increase of the sintering temperature from 950 to 1200 °C, the polarization resistance obtained at 800 °C increased from 0.12 to 0.56 $\Omega \text{ cm}^2$.

However, till now the morphology of the second phase developed during the fabrication has not been observed and how the insulating phases can affect the oxygen evolution reaction is still unclear. Consequently, in this part of the work, the possible reactions between LSCF and YSZ were firstly studied both in the form of powder mixture and in the process of half-cell fabrication. Secondly, the electrochemical responses under OCV and I - V curves of half-cells sintered at different temperatures were studied in details.

4.2 Experimental Details

The possible reactions between LSCF and YSZ were inspected in the following two ways. Firstly, the possible reactions were investigated in the form of powder mixture. Specifically, LSCF and YSZ powder were mixed by ball milling with zirconia balls in a weight ratio of 1:1 and die-pressed into pellets. These pellets were sintered at different temperatures, from 750 to 1200 °C with an interval of 50 °C, for 2 h in air, with a ramping rate of 5 °C min^{-1} . At last, the as-prepared pellets were characterized by XRD to check the possible reaction products. As a comparison, powder mixtures of LSCF and GDC were sintered and characterized in the same way.

Secondly, the interfacial reaction between LSCF electrodes and YSZ electrolytes during the half-cell fabrication was investigated. In details, a half-cell was fabricated following the same way indicated in Chapter III. Then, the electrochemical performances under OCV and I - V curves of the half-cells were obtained. At last, the LSCF electrodes were removed by ultrasound treatment in diluted nitric acid and the surfaces of the resulted YSZ electrolytes were subject to FESEM and XRD examination. In this way, the effect of the interfacial reaction on the oxygen reduction/evolution reaction can be investigated.

4.3 Reactions between LSCF and YSZ in Powder Mixture

Figure IV-1 shows the X-ray diffraction patterns of LSCF and YSZ 1:1 mixture sintered at different temperatures, 750–1200 °C with an interval of 50 °C, for 2 h in air. Lattice parameters of the phases presented are extracted from XRD data by commercial software TOPAS and listed in Table IV-1. For sample sintered at 750 °C, peaks representing cubic YSZ and rhombohedral LSCF phases can be clearly recognized, without any sign of second phase formation. As the sintering temperature increases to 800 °C, peaks corresponding to SrZrO_3 start to emerge and become more and more intensive with the increase of the sintering temperature, representing an increasing amount of SrZrO_3 formed at higher temperatures. In addition to SrZrO_3 , CoFe_2O_4 spinel also precipitated due to the loss of Sr element.

Figure IV-1 XRD patterns for the mixture of LSCF and YSZ with a weight ratio of 1:1 sintered at different temperatures, (a) from 750 to 950 °C and (b) from 1000 to 1200 °C.

As for LSCF perovskite phase, an increase of the lattice parameter can be observed (Table IV-1) from 750 to 900 °C due to the loss of Sr, which is in consistence with previous studies (Hansen et al., 2007). For samples sintered at 900 and 950 °C, emergence of another perovskite phase with larger lattice parameters during the sintering can be clearly seen. The exact composition of this phase, designated as LSCF2 in Figure IV-1 and Table IV-1, is unknown but it is highly possible to be doped LaFeO₃ due to the loss of Sr and Co. After

1000 °C, an increase of the lattice parameter of LSCF2 happened together with a decrease of the lattice parameter of SrZrO₃, indicating a mutual diffusion took place between these two phases forming a solid solution. No other second phase like La₂Zr₂O₇ was detected in this circumstance.

Table IV-1 Summary of lattice parameters extracted from XRD data of the five phases, YSZ, LSCF, LSCF2, SrZrO₃ and CoFe₂O₄ in the mixture of LSCF and YSZ sintered at different temperatures for 2 h

Sintering Tempera- ture/°C	YSZ (Cubic) a/Å	LSCF (Rhombohedral) a/Å c/Å		LSCF2 (Rhombohedral) a/Å c/Å		SrZrO ₃ (Cubic) a/Å	CoFe ₂ O ₄ (Cubic) a/Å
750	5.1408	5.5039	13.3986				
800	5.1409	5.5052	13.4056			4.0739	
850	5.1414	5.5093	13.4082			4.0761	8.3465
900	5.1557	5.5173	13.4297	5.5718	13.5329	4.0832	8.3838
950	5.1540	5.5160	13.4153	5.5964	13.5912	4.0757	8.3766
1000	5.1584			5.5988	13.6103	4.0723	8.3745
1050	5.1627			5.5912	13.7897	4.0667	8.3831
1100	5.1624			5.5984	13.8126	4.0603	8.3841
1150	5.1589			5.6331	13.7163	4.0484	8.3851
1200	5.1621			5.6480	13.7668	4.0379	8.3928

Figure IV-2 shows the X-ray diffraction patterns of LSCF and GDC 1:1 mixture sintered at different temperatures. It can be seen that at high sintering temperatures, the phase of LSCF and GDC are all well preserved, indicating that no reactions occurred between LSCF and GDC.

Figure IV-2 XRD patterns for the mixture of LSCF and GDC with a weight ratio of 1:1 sintered at different temperatures, (a) from 750 to 950 °C and (b) from 1000 to 1200 °C.

4.4 Reactions between LSCF and YSZ in Cell Fabrication

In the last section, the reaction between LSCF and YSZ has been studied in the form of powder mixture sintered at different temperatures. However, although that case is suitable in studying the possible reaction products, the morphological and compositional changes caused by the formation of SrZrO_3 second phase at the LSCF electrode–YSZ electrolyte interface are still unclear.

In this section, the surfaces of YSZ electrolytes were examined by XRD and SEM after the removal of LSCF electrodes.

Figure IV-3 shows the XRD patterns of the YSZ electrolyte surfaces after the removal of LSCF electrodes sintered at 800 °C (YL800), 900 °C (YL900) and 1000 °C (YL1000). No second phase was detected on YL800 and the formation of SrZrO_3 started from sintering temperature of 900 °C. This is tally with above study in powder mixture form.

Figure IV-3 XRD patterns of the YSZ electrolyte surfaces after the removal of LSCF electrodes sintered at (a) 800 °C (YL800), (b) 900 °C (YL900) and (c) 1000 °C (YL1000).

SEM images of the surfaces of YSZ electrolytes after the removal of LSCF electrodes of YL800, YL900 and YL1000 are shown in Figure IV-4. A bare YSZ electrolyte surface is also shown in Figure IV-4d for comparison, which is clean and YSZ grains can be clearly distinguishable. YL800 presents a similar YSZ electrolyte surface with a few bright particles, which could be the residue of LSCF electrode. In contrast, YSZ electrolyte surface of YL900 is partially

covered by some grey second phase particles. Furthermore, YSZ electrolyte surface of YL1000 is fully covered by a layer of second phase and YSZ grains cannot be observed. In combination with the above XRD study, it can be inferred that the layer is composed of SrZrO_3 second phase.

Figure IV-4 Surfaces of YSZ electrolytes after the removal of LSCF electrodes sintered at (a) 800 °C (YL800), (b) 900 °C (YL900) and (c) 1000 °C (YL1000); (d) Bare YSZ electrolyte surface.

Furthermore, it should be noted that the SrZrO_3 layer is rather dense without any visible holes and it covers the whole surface of the YSZ electrolyte as shown in Figure IV-4c. This morphology is quite different from the interface between LSM electrodes and YSZ electrolytes, where the formation of convex rings were observed (S. P. Jiang et al., 2005). This demonstrates that the interfacial reaction took place anywhere rather than being restricted to the

places where LSCF particles and the YSZ electrolyte were in contact, most likely due to the high diffusivity of Sr (F. Wang, M. E. Brito, et al., 2014; F. Wang, M. Nishi, et al., 2014).

4.5 Electrochemical Performances of LSCF Electrode Sintered at Different Temperatures

4.5.1 Electrochemical Impedance Responses of LSCF Electrodes Sintered at Different Temperatures under OCV

Figure IV-5a and b show the Nyquist and Bode plots, respectively, for half-cells with YSZ electrolytes obtained at 800 °C under OCV in air. The values of R_p are summarized in Figure IV-5c, in which an increase of 90 times, from 0.03 to 2.72 $\Omega \text{ cm}^2$, can be observed when the sintering temperature increases from 800 °C to 1000 °C. This increase is accompanied with decrease of the summit frequency as shown in the Bode plot in Figure IV-5b, representing an increasingly more pronounced low-frequency process. Besides, activation energy, E_a , for each cell has also been derived and showed a trend of decreasing as sintering temperature increases as shown in Figure IV-5d, demonstrating a shift of the reaction path. This also supports above analysis based on Bode plots that the low-frequency process becomes more prominent with the increase in sintering temperature.

Figure IV-5 (a) Nyquist and (b) Bode plots for half-cells with YSZ electrolytes sintered at different temperatures ranging from 800 to 1000 °C and tested at 800 °C under OCV; (c) Changes of polarization resistance, R_p , and (d) activation energy, E_a , with increasing sintering temperature

According to previous reports, the mechanisms accounting for the increase of R_p in LSCF can be categorized into three kinds: coarsening of the microstructure (Y. Liu et al., 2013; Shah et al., 2011), Sr segregation (S. P. Simner et al., 2006), and interfacial reactions between electrodes and electrolytes (Kindermann et al., 1996; Kostogloudis et al., 2000; F. Wang, M. Nishi, et al., 2014). Combining with above XRD results, it can be inferred that the formation of SrZrO_3 between LSCF and YSZ plays an important role in the increase of R_p with the increase of sintering temperature. As for the other two factors, coarsening of the microstructure and increased Sr surface segregation at higher sintering temperatures could also be part of the increase of R_p by retarding mass transfer process (H. Ding et al., 2013; W. Lee et al., 2013).

LSCF electrodes sintered on GDC electrolytes at different temperatures were also fabricated and tested to further figure out the effect of the sintering temperature. Nyquist plots of the EIS tests are shown in Figure IV-6a.

Comparison of R_p of LSCF electrodes sintered on YSZ or GDC electrolytes are plotted in Figure IV-6b. For GDC electrolyte, R_p increases by 47% from 0.0161 $\Omega \text{ cm}^2$ to 0.0237 $\Omega \text{ cm}^2$ as the sintering temperature increases from 800 $^{\circ}\text{C}$ to 1000 $^{\circ}\text{C}$. One may point out that the absolute values of the R_p of LSCF electrodes on GDC electrolytes are very low, which makes the results more vulnerable to the environmental effects. However, it is safe to say that the R_p are within the range of 0.01 ~ 0.05 $\Omega \text{ cm}^2$. In contrast, for YSZ electrolyte, R_p increases by 100 times from 0.0267 $\Omega \text{ cm}^2$ to 2.7219 $\Omega \text{ cm}^2$. Thus, the effect of the formation of the SrZrO_3 layer with the increase of sintering temperature is dominant in the increase of R_p , while the effect of the inherent changes of LSCF, i.e. particle size increase and Sr surface segregation, is negligible.

Figure IV-6 (a) Nyquist plots for half-cells with GDC electrolytes sintered at different temperatures ranging from 800 to 1000 $^{\circ}\text{C}$ and tested at 800 $^{\circ}\text{C}$ under OCV; (b) Changes of R_p with testing temperatures of LSCF electrodes sintered on YSZ or GDC electrolytes

Another experiment was also conducted on YL1000 to confirm the effect of the SrZrO_3 layer. A YL000 was tested at first. Then, the LSCF electrode was removed and again LSCF electrode was re-applied on the YSZ substrate and sintered at 800 °C. The inherent changes of LSCF electrodes are excluded by the lowing sintering temperature and the effect of SrZrO_3 layer can be concluded by comparing the performance of as-prepared YL1000 and the re-applied LSCF electrode. Figure IV-7 shows the comparison of R_p against testing temperature of YL1000 and the re-applied LSCF electrode sintered at 800 °C. The re-applied LSCF electrode only shows a slight improvement at lower testing temperatures, demonstrating that the high R_p of Y1000 is dominated by the formation of SrZrO_3 layer.

Figure IV-7 Changes of R_p along testing temperature for (a) YL1000 (Half-cells with LSCF electrodes sintered on YSZ electrolytes at 1000 °C) and (b) re-applied LSCF electrode sintering at 800 °C after the removal of LSCF electrode of YL1000

4.5.2 Current–Voltage Curves of LSCF Electrodes Sintered at Different Temperatures

I – V curves were obtained at 800 °C and are shown in Figure IV-8 for YL800, YL900, YL1000, GL800, GL900 and GL1000. It should be pointed out

that the I - V curves do not exclude the ohmic resistance from the electrolyte; thus, different samples cannot be directly compared. However, a comparison between the different modes of the same sample is viable. To make the comparison clear, Table IV-2 summarizes the voltage of each sample obtained at 1 A cm^{-2} for both modes.

Figure IV-8 I - V curves obtained at 800°C of LSCF electrodes sintered on YSZ or GDC electrolytes at different temperatures

Table IV-2 Voltage of each sample obtained at 1 A cm⁻² for both fuel cell and electrolyzer modes at 800 °C

Sample	Fuel Cell	Electrolyzer	Sample	Fuel Cell	Electrolyzer
YL800	1.32 V	−1.19 V	GL800	0.78 V	−0.78 V
YL900	1.73 V	−1.46 V	GL900	0.79 V	−0.74 V
YL1000	2.72 V	−1.51 V	GL1000	0.66 V	−0.64 V

For half-cells with GDC electrolytes, the performances of different modes are almost symmetrical despite of a slight asymmetric at high sintering temperatures. In comparison, the half-cells with YSZ electrolytes become more and more asymmetrical with the increase of sintering temperature. As above mentioned, the increase of sintering temperature can cause the generation of SrZrO₃ second phase and precipitation of spinel phase. Therefore, the asymmetrical behaviour could be related to the two phases. However, the exact reason is not clear.

4.6 Conclusion

In this part, the possible second phase formation between LSCF and YSZ was investigated. It was found by XRD that SrZrO₃ second phase could generate after sintering for 2 h at a sintering temperature equal to or higher than 850 °C, along with the precipitation of spinel phase. By SEM, the SrZrO₃ second phase of YL1000 was observed to cover the whole surface of the YSZ electrolyte, rather than being restricted to the places where the LSCF electrode was in contact with the YSZ electrolyte. In electrochemical characterization, the formation of SrZrO₃ at the LSCF–YSZ interface was demonstrated to cause significant increase of R_p . In addition, the SrZrO₃ second phase showed more evidence of negative effect on the fuel cell mode than on the electrolyzer mode.

Chapter V Degradation of LSCF Air Electrodes

under OCV at Elevated Temperatures

5.1 Introduction

In the last chapter, the reaction between LSCF and YSZ or GDC has been studied and it was shown that the interfacial reaction between LSCF electrodes and YSZ electrolytes can cause severe degradation on the performance of LSCF electrodes.

Apart from the performance corruption during the fabrication stage, the degradation of the LSCF electrode under SOEC operation condition is another obstacle needs to be overcome before SOEC can be exploited commercially. One of the major concerns for LSCF is the surface segregation of Sr (Wakako Araki et al., 2014; H. Ding et al., 2013; John Druce et al., 2014; Kubicek et al., 2011; W. Lee et al., 2013; Oh et al., 2012; Steve P Simner et al., 2006). The segregation of A-site dopants in perovskites as electrochemical catalyst is a critical concern as it may degrade the performance and cause structural changes. However, a consensus was still not reached on the driving force of the strontium segregation, its effect on the electrochemical performance and ways to suppress it.

Oh et al. (Oh et al., 2012) has shown the appearance of Sr-O based precipitation by Auger electron spectroscopy on the surface of LSCF annealed at elevated temperatures, 600–900 °C, for 100 h. Druce et al. (John Druce et al., 2014) also observed an increase of Sr concentration on the surface of LSCF after annealing the samples at 400, 600, and 800 °C for 8 h by means of Low energy ion scattering.

Effects of various factors on the Sr surface segregation have been investigated by several groups. Fister et al. (Fister et al., 2008) changed the oxygen partial pressure and observed that the strontium surface concentration of (001)-oriented $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ thin films increased with decreasing oxygen partial pressure, suggesting that the surface oxygen vacancy concentration plays a significant role in controlling the degree of segregation. Araki et al. (W. Araki et al., 2016; Wakako Araki et al., 2014) have applied mechanical stresses on LSCF bars and found that Sr surface segregation could be suppressed by applying compressive stress. This is supported by the first principle modelling conducted by Ding et al. (H. Ding et al., 2013). They found that applying compressive stress and reducing surface charge could mitigate the Sr surface segregation, which can be achieved through oxygen vacancy, Co substitution of Fe, and cation site deficiency. However, different conclusion was drawn by Kubicek et al. (Kubicek et al., 2013). Their experiment showed that the tensile lattice strain accelerated oxygen surface exchange and diffusion in $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ thin films, which was ascribed to the removal of surface Sr enrichment.

The driving force of the Sr surface segregation was studied by both experimental and computational methods by Lee et al. (W. Lee et al., 2013). They have systematically studied the mechanism of the segregation of A-site dopants on $\text{Ln}_{0.8}\text{D}_{0.2}\text{MnO}_{3-\delta}$ (host cation Ln = La, Sm; dopant D = Ba, Sr, Ca) and demonstrated that both elastic and electrostatic energy contributed to the A-site dopant surface segregation.

When it comes to the effect of Sr segregation on the electrochemical performance, previous studies do not reach a consensus. On thin film electrodes,

Baumann et al. (Baumann et al., 2005) have applied cathodic current (Fuel cell mode) on LSCF electrode and found that the current can significantly activate the electrode. With the aid of XPS, Sr concentration on the LSCF surface increased from 28 at. % to 42 at. % after cathodic treatment, while it remained at 28 at. % after anodic treatment. Thus, they have concluded that the surface concentrated Sr contributes to the activation of the LSCF electrode after cathodic treatment. However, this result contradicts the experiment done by Kubicek et al. (Cai et al., 2012; Kubicek et al., 2011). They found that the electrochemical performance of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ thin film electrode also fabricated by PLD degraded with annealing time, accompanied by the formation of ~1 nm Sr rich layer. After the removal of this layer by chemical etching, the performance was recovered to the initial level. Apart from the model thin film electrode, Simner et al. (Steve P Simner et al., 2006) ascribed the aging of the LSCF electrode operated in fuel cell mode to the Sr surface segregation as SrO was detected by XPS.

Consequently, a clear relationship between the emergence of surface Sr-based species and its effect on the performance of a porous LSCF electrode under a typical RSOC operating temperature has not yet been well established. It is necessary to fully understand the relationship between the degradation of the performance of a porous LSCF electrode and its surface compositional change at a typical RSOC operating temperature in the first place, to serve as a basis for the lifespan study under anodic current later. In this part, variations of the electrochemical performances of LSCF electrodes in half-cells at high temperature, 750 °C, under equilibrium potential were recorded by EIS and the corresponding surface chemical compositional changes were investigated by

XPS. Samples with nitric acid etching treatment were also examined to clearly verify the effect of surface compositional changes.

5.2 Experimental Details

In this part, a total of 9 half-cells were fabricated and tested under various conditions as summarized in Table V-1. The sintering temperature of the LSCF electrodes is 900 °C. Briefly, during the electrochemical characterization, sample 1–3 were tested at different temperatures, 650, 700 and 750 °C, without current for 24 h to study the performance change with time and the effect of testing temperature on it. Sample 4–5 were performed with nitric acid etching treatment. The detailed procedure of nitric acid etching treatment can be found in Chapter III. The aim of this step is to remove the possible surface components of LSCF particles in the electrode, as the possible metal oxide or metal salt formed on the surface is soluble in nitric acid. Thus, by comparing the performances of the electrodes with and without, before and after nitric acid treatment, the relation of surface precipitation substances and the electrochemical performance degradation can be clearly revealed. At last, sample 6–9 were used to conduct surface characterization technique, EDX and XPS, to study the surface compositional changes after different tests.

At last, YSZ and LSCF powder mixture, with a weight ratio of 1:1, was sintered at 750 °C for 100 h and examined by XRD to ensure that no second phase would form during the anneal at 750 °C and thus no synergistic effect of the formation of SrZrO_3 .

Table V-1 Summary of testing procedures for sample 1–9

Samples	Description	Testing condition	Nitric acid etching treatment	Testing condition	EDS	XPS	SEM
Sample 1	As-prepared YL900	24 h 750 °C OCV					✓
Sample 2	As-prepared YL900	24 h 700 °C OCV					
Sample 3	As-prepared YL900	24 h 650 °C OCV					
Sample 4	As-prepared YL900	0.1h 750 °C OCV	✓	24 h 750 °C OCV			
Sample 5	As-prepared YL900	24 h 750 °C OCV	✓	48 h 750 °C OCV			
Sample 6	Raw LSCF powder				✓	✓	
Sample 7	As-prepared YL900					✓	✓
Sample 8	As-prepared YL900	24 h 750 °C annealing				✓	
Sample 9	As-prepared YL900	24 h 750 °C annealing	✓			✓	

5.3 Electrochemical Response Evolutions of Half-Cells

Figure V-1 shows the Nyquist plot evolutions of sample 1–3 tested at different temperatures, 750, 700 and 650 °C, under OCV for 24 h. In the figure, $t = 0$ h is defined as the time when the first electrochemical test was conducted. As shown in Figure V-1a, R_s remains the same value during the test, while R_p increases gradually, which implies that the degradation mainly comes from the electrode. The same phenomena can be observed when the testing temperature was lowered down (Figure V-1b and c).

To further locate the origin of this increase in R_p , ADIS was performed (Jensen et al., 2007) and the results are shown in Figure V-2. From Figure V-2a, it can be observed that the increase of R_p comes from the change of a process happening at around 100 Hz. According to previous reports as introduced above, this process is referred as mass transfer process, or so-called “surface” process, including oxygen adsorption/desorption, dissociation/ association and diffusion, which happens at the gas-solid interface in electrode (Kammer Hansen et al., 2010; J.-W. Lee et al., 2009; Murray et al., 2002). Samples under lowered testing temperatures also show similar change in the plots (Figure V-2b and c). Thus, the gradual slower “surface” process during the tests would mean that the degradation of LSCF electrodes is caused by a change of surface property regardless of the testing temperature.

Degradation of LSCF Air Electrodes under OCV at Elevated Temperatures

Figure V-1 Electrochemical impedance spectroscopy evolutions of half-cells tested at (a) 750 °C (sample 1), (b) 700 °C (sample 2), and (c) 650 °C (sample 3) under OCV for 24 h ($t = 0$ h is defined as the time when the first electrochemical test was conducted)

Degradation of LSCF Air Electrodes under OCV at Elevated Temperatures

Figure V-2 ADIS plots for half-cells during test at (a) 750 °C (sample 1), (b) 700 °C (sample 2), and (c) 650 °C (sample 3) under OCV for 24 h

Figure V-3 displays the dependence of R_p increase with time and the square root of time. For easy comparison, the relative change of R_p , i.e. $R_p/R_{p,0}$, was used, instead of its absolute change. From Figure V-3b, the increase of R_p presents a linear dependence on the square root of time. This dependence was also observed previously by Constantin et al. (Constantin et al., 2013) on LSCF electrodes with YSZ as the electrolyte, implying that a diffusion process is involved in the degradation of the LSCF electrode, which is highly possible to be the Sr diffusion to the surface of LSCF particles (H. Ding et al., 2013). The slope of this linear dependence can be obtained from the linear fitting and can be regarded as an indicator of the degradation rate of LSCF electrodes. As indicated in the plot, the slope increases from 0.0139 to 0.1360 with the increase of testing temperature from 650 to 750 °C, meaning a faster degradation at higher testing temperature. Previous report (Oh et al., 2012) on the formation of surface Sr–O based second phase also presented a trend that at higher temperature more second phase emerged on the surfaces of LSCF pellets.

Figure V-3 Dependence of polarization resistance increase with (a) time and (b) square root of time for half-cells tested at 750 °C (sample 1), 700 °C (sample 2), and 650 °C (sample 3) under OCV for 24 h

5.4 Effect of Nitric Acid Etching Treatment

In this part, nitric acid etching treatment was employed to provide evidence for the effect of surface compositional changes on the degradation of LSCF electrodes. Two cells, sample 4 and 5, were treated with nitric acid following certain procedures as summarized in Table V-1. Sample 4 was tested for a few minutes at the beginning to obtain its initial performance. Then the sample was unloaded from the test station for nitric acid etching treatment followed by annealing test for another 24 h at 750 °C. For sample 5, it was tested at 750 °C for 24 h first, followed by nitric acid etching treatment and then testing for another 48 h.

Figure V-4 shows the dependence of R_p relative increase with the square root of time for sample 4 and 5. For the first 24 h, R_p of sample 4 decreased at first and then increased with a slope of 0.1276 by linear fitting, which is only slightly smaller than the value for sample 5, 0.1360, indicating a rather similar surface property of LSCF particles in freshly prepared electrodes with or without nitric acid treatment. However, for the last 48 h testing of sample 5, R_p at first decreased to a value smaller than that before acid treatment, but larger than initial measurement before 24 h testing, and then increased with a slope which is drastically reduced from the initial value of 0.1360 to 0.0706, meaning that the surface property of LSCF particles has changed during the first 24 h testing for sample 5. Note that R_p after the nitric acid etching treatment was slightly larger than that before the treatment. In addition, for both samples after the treatment, R_p decreased at first and then increased again. This could be explained by that the acidity would attack the surface of LSCF (Lou et al., 2010) and cause morphological changes, leading to a slight higher R_p immediately

after acid treatment. Then the morphology would be modified by the heat treatment during the initial period of test after acid treatment, resulting in decreased R_p during this period. Nonetheless, exact reasons accounting for this phenomenon need to be further investigated.

Figure V-4 Effect of nitric acid treatment on square root of time dependence of polarization resistance increases annealed at 750 °C for sample 4 and 5 (Sample 4 was tested to obtain its initial performance at the beginning, and then it was unloaded from the test station for nitric acid etching treatment followed by another 24 h testing at 750 °C; Sample 5 was tested at 750 °C for 24 h first, followed by nitric acid etching treatment and testing for another 48 h)

The changes on the R_p and degradation rate for sample 5 before and after the nitric acid treatment evidently reflect that the degradation of LSCF electrodes is caused by the change of surface composition. For sample 4 with freshly prepared LSCF electrode, only limited surface substance emerged, thus, the effect of nitric acid etching treatment was limited. While for sample 5 which

has been tested for 24 h, substantial surface substance presented, leading to a compromised performance. After the removal of surface substance by nitric acid, the performance improved and the degradation rate decreased. Similar effect of the etching treatment on the electrochemical performance has also been observed previously on model thin film electrode (Cai et al., 2012; Jung & Tuller, 2012; Kubicek et al., 2011). Jung et al. (Jung & Tuller, 2012) used 10% diluted buffered hydrofluoric acid to remove the surface layer on thin film $\text{SrTi}_{0.5}\text{Fe}_{0.5}\text{O}_{3-\delta}$ and observed reduced R_p after the etching tested at 485–560 °C. Kubicek et al. (Kubicek et al., 2011) and Cai et al. (Cai et al., 2012) used diluted hydrochloric acid to conduct chemical etching after testing $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ thin films at 600 °C under OCV for 72 h and obtained a reduced resistance which was lower than initial value before 72 h test but an accelerated degradation rate after etching treatment. However, in this work, the smallest R_p for sample 5 after acid treatment is still larger than initial measurement before 24 h test, which could be ascribed to the low pH value (pH ≈ 3) of the acid used, which can only dissolve segregated second phase but cannot remove the whole surface layer. Besides, another discrepancy is that the degradation rate after acid treatment is lower than that before treatment in this work as opposed to an accelerated degradation rate observed by Cai et al. (Cai et al., 2012), which needs further investigation.

5.5 XPS Studies

To further confirm the above conjecture, the composition of raw LSCF powder (sample 6) was checked by EDX and the surface compositions of LSCF particles in raw LSCF powder, freshly prepared LSCF electrode (sample 7), LSCF electrode after 24 h anneal (sample 8) and nitric acid treated LSCF

electrode after anneal (sample 9) were checked by XPS. The results are listed in Table V-2. The EDX result has confirmed that the bulk composition of LSCF raw material is 30 cation % for La, 20 cation % for Sr, 9 cation % for Co and 41 cation % for Fe, which is close to its stoichiometric ratio of 6:4:2:8. However, the XPS result of raw LSCF material shows that in the surface area of LSCF particles, the Sr concentration is 35 cation % (Sample 6). This is in consistence with previous observation (Y. Liu et al., 2014) that Sr tends to enrich at the surface area of LSCF particle. For freshly prepared LSCF electrode, Sr concentration detected by XPS increases to 45 cation % (Sample 7). After 24 h anneal, this value further rises to 54 cation % (Sample 8). Afterwards, nitric acid etching treatment reduces the Sr concentration to 37 cation % (Sample 9), close to the value of raw material. Moreover, above increase and decrease of Sr concentration is accompanied with decrease and increase of La and Fe concentration as can be observed in Table V-2, while Co concentration remains almost constant.

In order to check if there is any surface segregated Sr-based second phase other than LSCF perovskite, peak fitting was conducted on the XPS spectra of Sr as shown in Figure V-5. The Sr 3d spectrum showed a doublet state due to spin orbit, coupling of $3d_{3/2}$ and $3d_{5/2}$, as shown in the figure. Two pairs of Sr $3d_{3/2}$ and $3d_{5/2}$ couple can be extracted by peak fitting of the Sr 3d spectrum. The pair with lowering binding energy, ~133.5 eV for $3d_{3/2}$ and ~132 eV for $3d_{5/2}$, is identified as bulk-bound state Sr, denoted as Sr_B , in the lattice of LSCF perovskite oxide (Y. Liu et al., 2014). While the pair with higher binding energy, ~135.5 eV for $3d_{3/2}$ and ~133.9 eV for $3d_{5/2}$, is recognized as the surface Sr-containing component in this study, denoted as Sr_s , on the surface of LSCF particles in electrode (Baumann et al., 2005; Van Der Heide, 2002). This

“surface” component may include Sr^{2+} in the perovskite surface termination layer, and/or Sr-based second phase segregated. Concentrations of these two Sr states in LSCF electrode for the four samples, sample 6–9, are also summarized in Table V-2. For LSCF raw material, the ratio of Sr_S to Sr_B is 0.46 (Sample 6). Electrode sintering process increases this value to 0.80 (Sample 7). After 24 h annealing, this value reaches 1.00 (Sample 8). At last, nitric acid treatment reduces this value to 0.54 (Sample 9). Concentration variations of total Sr, Sr_S and Sr_B along the four samples are plotted in Figure V-6. From the figure, one can see that the increase of total Sr concentration originates from the increase of Sr_S , while the concentration of Sr_B almost remains constant.

Figure V-5 Peak fitting results of Sr spectra for (a) raw LSCF powder (sample 6), (b) freshly prepared LSCF electrode (sample 7), (c) LSCF electrode after 24 h annealing (sample 8), and (d) nitric acid treated LSCF electrode after annealing (sample 9)

Table V-2 Results of EDX and XPS for raw LSCF powder (Sample 6), freshly prepared LSCF electrode (Sample 7), LSCF electrode after 24 h annealing (Sample 8) and nitric acid treated LSCF electrode after annealing (Sample 9)

Element	EDX (cation %)		XPS (cation %)			
	Sample 6		Sample 6	Sample 7	Sample 8	Sample 9
La	30		29	21	21	24
Sr	20		35	45	54	37
Sr _S * 3d	3d _{3/2}	-	5	10	13	6
	3d _{5/2}	-	6	10	14	7
Sr _B * 3d	3d _{3/2}	-	12	12	13	12
	3d _{5/2}	-	12	13	14	12
Sr _S /Sr _B	-		0.46	0.80	1.00	0.54
Co	9		10	11	10	13
Fe	41		26	23	15	26

*: Sr_B denotes Sr in LSCF perovskite lattice; Sr_S denotes the surface Sr-containing component including Sr²⁺ in the perovskite surface termination layer, and/or Sr-based second phase.

Figure V-6 Concentration variations of total Sr, Sr_S and Sr_B along sample 6-9 (sample 6, raw LSCF powder; sample 7, freshly prepared LSCF electrode; sample 8, LSCF electrode after 24 h annealing; sample 9, nitric acid treated LSCF electrode after annealing)

Combining the XPS results with above electrochemical characterization, one can see that the evolution of the polarization resistance is accompanied with the change of “surface” Sr-containing component. That is, the polarization resistance increases along with the increase of Sr_s , and the polarization resistance and degradation rate decrease as the decrease of Sr_s . According to previous reports (Choi et al., 2013; Kawada et al., 2002), increasing Sr in $La_{1-x}Sr_xCoO_{3-\delta}$ and LSCF perovskite phase will lead to higher oxygen reduction reaction activity. Thus, it is reasonable to say that the increase of Sr-based second phase dominates the increase of Sr_s over the enrichment of Sr in the termination layer in this work. Otherwise, the performance would be improved by the Sr enrichment in the termination layer of perovskite phase other than degrade during the test.

5.6 SEM and XRD Studies

SEM images of the top views of LSCF electrodes were taken before and after 24h testing at 750 °C as presented in Figure V-7. There is no observable change on the microstructure and particle size. Besides, XRD spectrum of LSCF and YSZ powder mixture sintered at 750 °C for 100 h was taken and shown in Figure V-8. From the spectrum, one can see that there is no second phase like $SrZrO_3$ detected. These results eliminate possible synergistic effects of microstructural changes and interfacial reactions on the degradation of LSCF electrodes.

Figure V-7 SEM top views of LSCF electrode (a) before (sample 7, freshly prepared LSCF electrode) and (b) after (sample 1, half-cell tested at 750 °C) 24 h testing

Figure V-8 XRD pattern of YSZ and LSCF powder mixture with a weight ratio of 1:1 sintered for 100 h at 750 °C

5.7 Discussion

Consequently, from the results obtained, it can be concluded that the degradation of LSCF electrode under OCV at elevated temperature arises from the out-diffusion of lattice Sr to the surface and segregated as second phase on the LSCF electrode. Schematic illustrations of the surface compositional change of the LSCF particles in electrode for sample 5 are shown in Figure V-9. For raw LSCF materials, the surface area is enriched with Sr, as well as little Sr-based second phase (Figure V-9a). During the fabrication process, surface second phase increases slightly (Figure V-9b). However, the 24 h test will further out-diffuse the Sr from the bulk to the surface of LSCF particle and segregated as second phase (Figure V-9c), degrading the performance. In the course of fabrication and test, bulk LSCF has become Sr-deficient due to out-diffusion of Sr (Figure V-9c). At last, nitric acid washes the surface Sr-based second phase off (Figure V-9d), which improves the performance of electrode.

Besides, the degradation is also slowed down since the Sr out-diffusion is decelerated as a result of the reduction of Sr content in the bulk of LSCF, which makes the doped Sr less likely to diffuse out. This surface second phase can be inferred as SrO and/or as reaction products formed with chemi-absorbed gases (SrCO_3 or $\text{Sr}(\text{OH})_2 \cdot x\text{H}_2\text{O}$), since the concentrations of all the elements detected by XPS decrease except for Sr during the annealing. The above results support the conclusion (Kubicek et al., 2011; Steve P Simner et al., 2006) that surface Sr-based species is detrimental to the electrochemical performance of a porous LSCF electrode.

Figure V-9 Schematic illustrations of the surface compositional change of the LSCF particles for sample 5 during fabrication and testing: (a) for raw LSCF materials, surface is enriched with Sr as well as little Sr-based second phase; (b) for freshly prepared electrode, surface Sr-based second phase increases a bit; (c) for electrode after testing for 24 h, surface Sr-based second phase increases again, while the bulk LSCF become Sr-deficient due to the Sr out-diffusion; (d) for nitric acid treated electrode, surface Sr-based second phase reduces to the level comparable to raw material

5.8 Conclusion

The degradation mechanism of LSCF air electrodes was inspected under OCV at 750 °C. It has been found that the increase of R_p of LSCF under OCV condition showed a linear dependence on the square root of time. ADIS analysis demonstrated that this increase mainly comes from the change of

process happening at around 100 Hz, which was previously identified as mass transfer process. A comparison of the behaviours of the sample before and after nitric acid etching treatment showed that the degradation rate after nitric acid etching treatment has been dramatically reduced compared to the one before the treatment, indicating that the degradation is most likely due to the emergence of surface inhibited species on the LSCF electrode, which can be removed by nitric acid treatment. XPS examination showed that the “surface” Sr, including Sr^{2+} in the perovskite termination layer and Sr-based second phase like SrO , and/or the reaction products formed with chemi-absorbed gases ($\text{Sr}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ and SrCO_3), increased upon the annealing test and decreased upon the nitric acid etching treatment. Furthermore, SEM and XRD studies eliminate the possible synergistic effects of microstructural changes and interfacial reactions between LSCF and YSZ on the degradation. Based on these results, the degradation of LSCF electrodes under OCV can be concluded to be the result of surface segregation of Sr-based species, which retards the mass transfer process, including oxygen surface adsorption/desorption, surface dissociation/association and surface diffusion. This confirms the detrimental role of surface Sr-based second phase on the electrochemical performance of LSCF electrodes.

Chapter VI Electrochemical Behaviours of LSCF Air

Electrodes under Electrolysis Current

6.1 Introduction

In the last chapter, the degradation of LSCF air electrodes at 750 °C without the passage of electrolysis current was found to be related to the Sr out-diffusion and surface segregation. Subsequently, the degradation of LSCF electrodes under electrolysis current needs to be studied. Although several groups have conducted long-term tests on a full cells to study the stability, till now no electrolysis tests has been carried out on half-cells. As pointed out in the Literature Review, the tests on full cells cannot clearly reveal the relationship between the performance variations and the observed materials changes, due to the complexity of a full cell. Thus, a basic understanding on the effect of the electrolysis current on the electrochemical behaviour and material property of LSCF electrodes is still lacking.

In this part, the effects of the electrolysis current on the electrochemical behaviours of LSCF air electrodes applied on YSZ electrolytes are presented.

6.2 Experimental Details

Half-cells with LSCF electrodes sintered at 800 °C (YL800), 900 °C (YL900), 950 °C (YL950) and 1000 °C (YL1000) were tested in different conditions listed in Table VI-1.

Table VI-1 Electrolysis test conditions for half-cells sintered on YSZ electrolytes at different temperatures: 800 °C (YL800), 900 °C (YL900), 950 °C (YL950) and 1000 °C (YL1000)

Samples	Description	Electrolysis testing condition*
YL800	Half-cell with LSCF electrode sintered at 800 °C and YSZ electrolyte	a. 0.2 A cm ⁻² for 48 h at 800 °C
YL900	Half-cell with LSCF electrode sintered at 900 °C and YSZ electrolyte	0.2 A cm ⁻² for 34 h → 0.5 A cm ⁻² for 7 h → 1 A cm ⁻² for 5 h → 1.5 A cm ⁻² for 2 h → 2 A cm ⁻² for 2 h at 800 °C
YL950	Half-cell with LSCF electrode sintered at 950 °C and YSZ electrolyte	0.2 A cm ⁻² for 120 min at 800 °C
YL1000	Half-cell with LSCF electrode sintered at 1000 °C and YSZ electrolyte	a. 0.2 A cm ⁻² for 120 min at 800 °C b. 0.2 A cm ⁻² for 8 h → OCV for 14 h → 0.2 A cm ⁻² for 14 h → 1 A cm ⁻² for 14 h → OCV for 14 h → 1 A cm ⁻² for 15 h → 0.2 A cm ⁻² for 50 h at 800 °C

*: a and b means different cells; → means different operating conditions on one cell tested successively; OCV means open circuit voltage, that is, no electrolysis current was applied.

6.3 Electrode Behaviours under Anodic Current of 0.2 A cm⁻²

Figure VI-1 shows the variations of R_p as a function of time (Figure VI-1a, c, e, g) and square root of time (Figure VI-1b, d, f, h) of half-cells polarized under anodic current density of 0.2 A cm⁻² at 800 °C. During the tests, the anodic current was interrupted from time to time and R_p were extracted under OCV. In the figure, all the data are quite regular except for sample YL800, because R_p of YL800 is relatively small, making it more vulnerable to environmental noises. The initial R_p extracted from the figure are 0.05, 0.25,

1.28 and 2.13 $\Omega \text{ cm}^2$ for electrodes sintered at 800, 900, 950 and 1000 $^{\circ}\text{C}$, respectively. At the beginning of the operation under anodic polarization of 0.2 A cm^{-2} , a turning point of sintering temperature can be easily spotted in between 900 $^{\circ}\text{C}$ and 950 $^{\circ}\text{C}$. Below this critical temperature, R_p of YL800 (Figure VI-1g) and YL900 (Figure VI-1e) increased with time for around 20 h, while R_p of YL950 (Figure VI-1c) and YL1000 (Figure VI-1a) decreased upon polarization treatment for around 60 min. But for all the four samples, R_p eventually stabilized after initial changes, at 0.21, 0.68, 0.90 and 1.42 $\Omega \text{ cm}^2$, respectively. In contrary, R_p increased constantly during annealing under OCV condition at elevated temperature as reported previously (Constantin et al., 2013). Thus, the application of anodic current may lead to the stabilization of LSCF electrode. This will be discussed in details below.

Figure VI-1 Variation of polarization resistance, R_p , tested under OCV at 800 °C as a function of (a, c, e, g) time and (b, d, f, h) square root of time of LSCF electrode sintered at (a, b) 1000, (c, d) 950, (e, f) 900 and (g, h) 800 °C on YSZ electrolytes polarized under an anodic current density of 0.2 A cm⁻² (In left column, dots are experimental data and lines are guidance to eyes; in right column, dots are experimental data and lines are linear fitting)

To further locate the origin of R_p variations, DRT analysis was performed on YL900 and YL950 to identify the peaks affected by the passage of the

electrolysis current. The results are shown in Figure VI-2. Peak intensity of high- and low-frequency processes were also extracted and are plotted against testing duration. For YL950 in Figure VI-2a and b, an obvious shrinkage of low-frequency peak can be observed in the first 30 min. After that, the curve remains the same for the rest 90 min. For YL900 in Figure VI-2c and d, the intensity of the low-frequency peak keeps increasing during the 20 h test with electrolysis current of 0.2 A cm^{-2} . This indicates that both the increase of R_P of YL900 and the decrease of R_P of YL950 come from the process represented by low-frequency peak in DRT analysis.

Figure VI-2 (a) DRT analysis and (b) DRT peak intensity evolution of YL950 (Half-cells with LSCF electrodes sintered on YSZ electrolytes at 950°C) during electrolysis test at 800°C under 0.2 A cm^{-2} ; (c) DRT analysis and (d) DRT peak intensity evolution of YL900 (Half-cells with LSCF electrodes sintered on YSZ electrolytes at 900°C) during electrolysis test at 800°C under 0.2 , 0.5 and 1 A cm^{-2}

Accordingly, electrochemical impedance responses of YL900 and YL950 were also fitted with equivalent circuit of $LR_S(CPE_H R_{P,H})(CPE_L R_{P,L})$. Fitting parameters for all the electrochemical impedances of YL900 and YL950 are listed respectively in Table VI-2 and Table VI-3. Changes of $R_{P,H}$ and $R_{P,L}$ for YL900 and YL950 as a function of time are also shown in Figure VI-1c and Figure VI-1e, respectively. The fitting results also reveal that the change of R_P comes from the change of $R_{P,L}$, while $R_{P,H}$ remains almost constant during the polarization. All the above analysis indicate that the changes of R_P originate from the change of the same property of LSCF electrodes, a property which can affect the mass transfer process for YL900 and YL950 in spite of different initial behaviours upon passing of anodic current.

In addition, dependences of the above variations of R_P on square root of time are presented in Figure VI-1b, d, f and h. The change of R_P was characterized by a linear dependence on the square root of time no matter R_P increased or decreased. In the last chapter, a linear increase of R_P on the square root of time during the annealing test under OCV condition has also been observed, and this was confirmed by X-ray photoelectron spectroscopy to be caused by the Sr out-diffusion and surface segregation. Thus, for this behaviour under current, a linear dependence may underline the same reason, i.e. Sr diffusion.

Table VI-2 Fitted impedance parameters of YL900 (Half-cells with LSCF electrodes sintered on YSZ electrolytes at 900 °C) tested at open circuit during anodic polarization at different current densities at 800 °C

Time/ h	Applied Anodic Current*/ A cm ⁻²	High Frequency Arc			Low Frequency Arc		
		$R_{P,H}/$ $\Omega \text{ cm}^2$	$Y_{0,H}/$ $\Omega^{-1} \text{ cm}^{-2} \text{ s}^{-n}$	n_H	$R_{P,L}/$ $\Omega \text{ cm}^2$	$Y_{0,L}/$ $\Omega^{-1} \text{ cm}^{-2} \text{ s}^{-n}$	n_L
0	0.2	0.22	3.25×10^{-3}	0.67	0.03	4.55×10^{-3}	1.07
2		0.18	4.52×10^{-3}	0.62	0.21	2.61×10^{-3}	0.84
5		0.20	9.54×10^{-3}	0.55	0.26	2.12×10^{-3}	0.89
8		0.21	1.56×10^{-2}	0.51	0.33	2.72×10^{-3}	0.88
12		0.22	1.96×10^{-2}	0.50	0.39	4.08×10^{-3}	0.85
16		0.22	2.50×10^{-2}	0.49	0.43	6.01×10^{-3}	0.83
20		0.22	2.27×10^{-2}	0.51	0.45	8.15×10^{-3}	0.81
24		0.23	2.32×10^{-2}	0.50	0.46	1.19×10^{-2}	0.78
28		0.24	2.50×10^{-2}	0.51	0.44	1.63×10^{-2}	0.76
32		0.24	2.21×10^{-2}	0.50	0.44	1.77×10^{-2}	0.74
34	0.5**	0.20	2.94×10^{-2}	0.51	0.28	3.13×10^{-3}	0.82
39		0.21	4.16×10^{-2}	0.48	0.25	2.51×10^{-3}	0.87
41	1	0.19	4.21×10^{-2}	0.51	0.20	2.13×10^{-3}	0.91
44		0.20	4.51×10^{-2}	0.50	0.19	1.92×10^{-3}	0.94
45	1.5	0.19	4.83×10^{-2}	0.51	0.17	1.74×10^{-3}	0.95
46		0.19	7.95×10^{-2}	0.47	0.18	1.81×10^{-3}	0.94
47	2	0.20	8.32×10^{-2}	0.47	0.18	1.76×10^{-3}	0.94
48		0.20	5.12×10^{-2}	0.51	0.18	1.80×10^{-3}	0.94

*: Applied current was interrupted at indicated time to perform EIS test.

**: Indicated current started after last test, meaning that 0.5 A cm⁻² started from $t = 32$ h in this case.

Table VI-3 Fitted impedance parameters of YL950 (Half-cells with LSCF electrodes sintered on YSZ electrolytes at 950 °C) tested at open circuit during anodic polarization at 0.2 A cm⁻² at 800 °C

Time/ h	Applied Anodic current*/ A cm ⁻²	High Frequency Arc			Low Frequency Arc		
		$R_{P,H}/$ $\Omega \text{ cm}^2$	$Y_{0,H}/$ $\Omega^{-1} \text{ cm}^{-2} \text{ s}^{-n}$	n_H	$R_{P,L}/$ $\Omega \text{ cm}^2$	$Y_{0,L}/$ $\Omega^{-1} \text{ cm}^{-2} \text{ s}^{-n}$	n_L
0	0.2	0.22	1.35×10^{-3}	0.73	1.06	8.08×10^{-4}	0.84
5		0.18	2.41×10^{-3}	0.68	0.99	8.72×10^{-4}	0.83
15		0.16	2.96×10^{-3}	0.66	0.92	9.37×10^{-4}	0.83
30		0.16	2.47×10^{-3}	0.66	0.85	1.04×10^{-3}	0.82
60		0.17	3.74×10^{-3}	0.65	0.73	1.25×10^{-3}	0.81
90		0.16	3.77×10^{-3}	0.65	0.71	1.24×10^{-3}	0.82
120		0.20	6.14×10^{-3}	0.61	0.70	1.52×10^{-3}	0.81

*: Applied current was interrupted at indicated time to perform EIS test.

6.4 Electrode Behaviours under Increasing Anodic Current

In Figure VI-3, the changes of R_P of YL900 polarized under an increasing anodic current at 800 °C, starting from 0.2 A cm⁻² followed by 0.5, 1, 1.5 and 2 A cm⁻² successively, are presented. The evolution of R_P was divided into six regions as indicated in the figure by roman numerical. It can be observed that R_P started with 0.25 $\Omega \text{ cm}^2$ at $t = 0$ h. During the operation under anodic current density of 0.2 A cm⁻², R_P gradually increased to 0.68 $\Omega \text{ cm}^2$ during the first 20 h (Region I). After that, R_P stabilized at that value for 14 h (Region II). From $t = 34$ h, a higher anodic current of 0.5 A cm⁻² was applied. As a consequence, R_P decreased and reached 0.46 $\Omega \text{ cm}^2$ at $t = 39$ h (Region III). Subsequently, R_P decreased again to 0.39 $\Omega \text{ cm}^2$ under polarization of 1 A cm⁻² (Region IV). This phenomenon continued to have effect until the current density reached 1.5 A cm⁻². At this time, R_P reached 0.36 $\Omega \text{ cm}^2$ (Region V), which is close to the initial performance. Afterwards, a limitation has been reached and the increase

of current density to 2 A cm^{-2} did not cause any decrease in R_P (Region VI) but a slight increase emerged, which could be a sign of the degradation of LSCF electrode at high current. Again, changes of R_P mainly came from low-frequency process, no matter R_P increased or decreased, according to the DRT analysis in Figure VI-2d and equivalent curve fitting results shown in Table VI-2 and Figure VI-3.

Figure VI-3 Variation of polarization resistance (R_P) obtained under OCV at $800 \text{ }^\circ\text{C}$ as a function of time for sample YL900 (Half-cells with LSCF electrodes sintered on YSZ electrolytes at $900 \text{ }^\circ\text{C}$) polarized under an increasing anodic current density from 0.2 to 2 A cm^{-2} (In the figure, dots are experimental data and lines are guidance to eyes)

6.5 Discussion

As mentioned above, the degradation of LSCF electrodes could be ascribed to either the formation of second insulated phase or the segregation of SrO. Thus, above suppression of the degradation or even activation upon the passage of electrolysis current can be possible explained by the following two

reasons. The first one is the re-incorporation of the out-diffused Sr back into the LSCF lattice. The second one is the activation of the SrZrO_3 layer formed during the fabrication stage.

As for the Sr re-incorporation, previously, Fister et al. (Fister et al., 2008) has done an in-situ characterization on the surface of LSM and found that the strontium surface concentration increased with decreasing oxygen partial pressure, suggesting that the surface oxygen vacancy concentration plays a significant role in controlling the degree of segregation, as the increasing concentration of positively charged oxygen vacancies near the surface may favour a high concentration of Sr near the surface to substitute La for local electroneutrality. Besides, modelling work done by Ding et al. (H. Ding et al., 2013) supports the above-mentioned experimental observations. Systematic first principles calculations showed that oxygen vacancy can enhance Sr surface segregation by driving the more positively charged LaO layer next to the surface, leaving Sr behind to form the Sr-rich surface. In addition, thermodynamic analysis done by Yokokawa et al. (Yokokawa et al., 2008) demonstrated that increasing oxygen partial pressure would lead to decrease in Sr activity.

It is well known that with the increase of oxygen partial pressure, concentration of oxygen vacancies in LSCF lattice will decrease (Jun et al., 2013). Based on above information, the high oxygen partial pressure generated by application of anodic current may decrease oxygen vacancies and be able to suppress the Sr surface segregation, which in turn would mitigate the formation of SrZrO_3 . To extrapolate, the authors speculate that an even higher oxygen

partial pressure could drive the Sr diffuse back into the LSCF lattice, leading to improved performance.

Consequently, a conjecture based on the Sr re-incorporation about the above observed R_P variations of half-cells upon the application of anodic current is described as follows. For sample YL900 shown in Figure VI-3, at the beginning, an anodic current density of 0.2 A cm^{-2} could create a certain oxygen partial pressure in the LSCF electrode, which maintained the amount of oxygen vacancies in LSCF phase to a certain value. This, in turn, restricted the Sr surface segregation, as well as the formation of SrZrO_3 , to a certain extent, as reflected by the stabilized performance after test for 20 h shown in Figure VI-3. After that, higher oxygen partial pressure was generated by the increase of anodic current, which reduced the amount of oxygen vacancies in LSCF phase. Thus, R_P was reduced due to that the Sr surface segregation was mitigated by Sr in-diffusion according to above analysis. As for the initial decreases of R_P for YL950 and YL1000 under 0.2 A cm^{-2} , it is because that the high sintering temperatures for these two samples have already caused more significant Sr surface segregation and SrZrO_3 formation than YL900 and YL800, which can be mitigated by being polarized with an anodic current density of only 0.2 A cm^{-2} . These explanations also tally with our above observation that the change of R_P always followed a linear dependence on the square root of time, a sign of Sr diffusion (Constantin et al., 2013), no matter it increased or decreased.

Another possible explanation is based on the activation of SrZrO_3 second phase at the electrode–electrolyte interface during the electrolysis test. However, this conjecture is only based on the initial performance and its relation with the

formation of SrZrO_3 . In Chapter IV, it has been demonstrated that the significant increase of R_P with the increase of sintering temperature of LSCF electrode on the YSZ electrolyte is related to the formation of SrZrO_3 . Thus, it is possible that the electrolysis current has caused some activation phenomenon on the SrZrO_3 layer which improved the performance. However, this improvement has not been studied before and the exact mechanism is not clear. Yokokawa has reported that the formation of $\text{La}_2\text{Zr}_2\text{O}_7$ is favourable at places where the oxygen partial pressure is high (Yokokawa, 2003). Thus, during the fuel cell operation of LSM air electrodes on YSZ electrolytes, the $\text{La}_2\text{Zr}_2\text{O}_7$ second phase tends to move away from the reaction sites where the oxygen is depleted due to the reaction. Nonetheless, in our case how the electrolysis current can affect the SrZrO_3 second phase is not clear.

To fully understand the effect of anodic current, in-situ surface compositional detection instrument, like in-situ X-ray photoelectron spectroscopy, needs to be employed to obtain real-time surface composition of LSCF particles at the electrode–electrolyte interface.

6.6 Short-term Test under Alternate Applied Anodic Current on YL1000 (Half-Cells with LSCF Electrodes Sintered on YSZ Electrolytes at 1000 °C)

At last, a short-term test was conducted on YL1000 under alternate applied anodic current for up to 129 h at 800 °C. The variations of R_P and R_S are shown in Figure VI-4. The figure is divided into seven regions according to the current density applied as indicated by the roman numerical. From the figure, one can see that R_P decreased upon a higher anodic current density, as in region I, region III, region IV and region VI, while increased upon a lower anodic

current density or OCV, as in region II, region V and region VII. This result again demonstrates that R_P can be affected by the application of different anodic current density and a higher anodic current had an activation effect and lowered the polarization resistance. In addition, one can see that for the last few hours, R_P stabilized at around $1.65 \Omega \text{ cm}^2$ (Point B). Comparing with point A, $R_P = 1.61 \Omega \text{ cm}^2$, there is no evident degradation on R_P before and after the test. In contrast, constant increase of R_S presented, with a few fluctuations of R_S upon the change of current density which are caused by the slight temperature changes.

Figure VI-4 Variation of R_P and R_S obtained under OCV at 800°C as a function of time for sample YL1000 (Half-cells with LSCF electrodes sintered on YSZ electrolytes at 1000°C) polarized under an alternate applied anodic current density (In the figure, dots are experimental data and lines are guidance to eyes)

SEM coupled with EDX was conducted to inspect possible microstructural or compositional changes after the test as shown in Figure VI-5 and Figure VI-6. Figure VI-5a, b and c show the SEM images of the LSCF electrode, the

electrode–electrolyte interface, the electrolyte where is near the interface of YL1000 respectively before the test, while Figure VI-5d, e and f show the corresponding images after test. The figure demonstrated similar microstructures before and after test for the LSCF electrode (Figure VI-5a and 6d) and the electrolyte (Figure VI-5c and f) of YL1000. However, delamination of the LSCF electrode appeared at some places after test (Figure VI-5e), with the formation of a thin dense layer at the interface. EDX examination was conducted on the layer as indicated by the red dot in Figure VI-5e. Figure VI-6 shows that there is substantial amount of Zr element in the layer and the amount of Sr element also exceeds its stoichiometry value in LSCF. Thus, it is highly possible that this layer was densified by the formation of insulated phase, SrZrO_3 , during the fabrication and testing process. As a result, this dense layer prevented the oxygen generated from diffusing out to the atmosphere and caused high oxygen partial pressure to build up between this dense layer and the electrolyte. Consequently, the observed delamination phenomenon occurred.

Figure VI-5 SEM images of sample YL1000 (Half-cells with LSCF electrodes sintered on YSZ electrolytes at 1000 °C) (a, b, c) before and (d, e, f) after short-term test. ((a, d): LSCF electrode; (b, e): electrode-electrolyte interface; (c, f): electrolyte near interface)

Figure VI-6 EDX result of the spot indicated by the red dot in Figure VI-5

6.7 Conclusion

In this chapter, the electrochemical performance evolutions of LSCF air electrodes under anodic current were reported. It was shown that the application of anodic current of 0.2 A cm^{-2} at 800°C could stabilize the performance of the LSCF electrode sintered at 900°C (YL900). In contrast, previous reports showed that R_p increased constantly under OCV condition as a result of Sr segregation. Furthermore, increasing anodic current to 0.5 A cm^{-2} and 1 A cm^{-2} rendered a continuous decrease of R_p after it had stabilized under 0.2 A cm^{-2} . The mechanism accounting for this phenomenon is not clear at this moment, but it could be related to the re-incorporation of the surface segregated Sr or the activation of the SrZrO_3 second phase. Further experiments are needed to investigate the underlying physics. At last, a short-term test under various anodic current on YL1000 again demonstrated that R_p varied with the alternate applied electrolysis current. After the test, delamination of the LSCF electrode can be observed.

Chapter VII Activation and Delamination

Mechanism of LSCF Electrodes under High-Current Electrolysis

7.1 Introduction

In the last chapter, the anodic current was found to have an activation effect on YL950 and YL1000. In addition, SEM images revealed that the LSCF electrode of YL1000 delaminated after the short-term test for 129 h under alternate applied electrolysis current. To further inspect the underlying physics, the activation and degradation of YL1000 was studied.

7.2 Experimental Details

YL1000 was fabricated and tested at 800 °C under electrolysis current of 1 A cm⁻². The current was purposely selected instead of 0.2 A cm⁻² in order to accelerate the change of LSCF electrodes and thus the changes would be easier to observe. Apart from YL1000, YL800 was also tested for comparison. Detailed analysis on the EIS curves were performed, including DRT analysis and equivalent curve fitting. Changes of activation energy were also calculated and plotted.

After different durations of electrolysis tests, SEM images and EDX analysis were taken to characterize the surfaces of YSZ electrolytes that were in contact with LSCF electrodes. The LSCF electrodes either have delaminated from the YSZ electrolytes or have been removed by diluted nitric acid as described in Experimental Procedure. In this way, the changes of the YSZ–LSCF interface can be associated with the changes of the electrochemical performance of LSCF electrodes after different testing durations.

7.3 Electrode Behaviours under Anodic Current of 1 A cm^{-2}

Figure VII-1 and Figure VII-2 show the electrochemical behaviours of YL1000 and YL800, respectively, during the electrolysis test with an electrolysis current of 1 A cm^{-2} at 800°C for 24 h. Figure VII-1a is the Nyquist plot showing the impedance evolution of the YL1000. The changes of R_P and R_S , as well as the change of the voltage, were extracted and drawn in Figure VII-1b. The evolution of the voltage and the resistances shows a pattern that can be resolved into three distinctive regions as indicated in the figure. At the beginning, the R_P and R_S were 1.53 and $1.66 \Omega \text{ cm}^2$, respectively. In region I, a substantial activation took place within 30 min, during which R_P decreased from 1.53 to $0.59 \Omega \text{ cm}^2$, while R_S decreased slightly from 1.66 to $1.52 \Omega \text{ cm}^2$. This initial activation behaviour is in consistence with the observation made in the last chapter on LSCF air electrodes.

After the initial activation period, R_S became relatively stable, increasing slightly from 1.52 to $1.56 \Omega \text{ cm}^2$ in region II. At the same time, R_P further decreased from 0.59 to $0.29 \Omega \text{ cm}^2$ in 17.5 h, demonstrating a slower decreasing rate compared with that in region I. Subsequently, in region III, R_S increased notably from 1.56 to $2.00 \Omega \text{ cm}^2$ within 6 h and R_P increased to $0.32 \Omega \text{ cm}^2$. After the test, the LSCF electrode delaminated from the YSZ electrolyte as shown in the cross-section SEM image in Figure VII-3a. It should be noted that in our test station, the sample was held between two vertical alumina rods. Thus, although the electrode delaminated, it was still pressed onto the YSZ electrolyte by the upper alumina rod, enabling EIS tests. The delamination phenomenon is in accordance with the increase of R_S and R_P as the contact between the LSCF electrode and the YSZ electrolyte was weakened.

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Mechanism of LSCF Electrodes under High-Current Electrolysis

Figure VII-1 (a) Evolution of Nyquist plot obtained under OCV, (b) evolution of voltage and resistances (c) DRT analysis of YL1000 (Half-cells with LSCF electrodes sintered on YSZ electrolytes at 1000 °C) during electrolysis with a current of 1 A cm⁻² at 800 °C for 24 h.

Figure VII-2 (a) Evolution of Nyquist plot obtained under OCV, (b) evolution of voltage and resistances (c) DRT analysis of YL800 (Half-cells with LSCF electrodes sintered on YSZ electrolytes at 800°C) during electrolysis with a current of 1 A cm^{-2} at 800°C for 24 h.

For comparison purpose, the YL800 underwent the same electrolysis test for 24 h and the results are shown in Figure VII-2. As can be seen in Figure VII-2a, the initial R_p and R_s of YL800 were 0.14 and 1.87 $\Omega \text{ cm}^2$, respectively. The electrochemical behaviour of YL800 during the test was also divided into three regions in the same way as YL1000 was. Two differences can be identified between YL1000 and YL800 in the electrochemical behaviour. Firstly, no significant activation process happened on R_p of YL800. Secondly, at the end of test, R_s of YL1000 increased abruptly while R_s of YL800 did not. After unloading YL800, one can see no electrode delamination of YL800 as shown in Figure VII-3b, in accordance with the more stable R_s . This also indicates that the delamination did not occur during the sample cooling and unloading process.

Figure VII-3 Cross-section images of (a) YL1000 (Half-cells with LSCF electrodes sintered on YSZ electrolytes at 1000 °C) and (b) YL800 (Half-cells with LSCF electrodes sintered on YSZ electrolytes at 800 °C) after the electrolysis test under 1 A cm⁻² at 800 °C for 24 h.

To study the activation process of YL1000 in details, DRTs (Schichlein et al., 2002) of the impedance curves were calculated and the results are presented in Figure VII-1c and Figure VII-2c for YL1000 and YL800, respectively, for the first 2 h of the electrolysis test. In Figure VII-2c, the DRT analysis of YL800 at the beginning of the electrolysis test shows a main peak at 6×10^2 Hz

(denoted as medium-frequency arc in the figure, M) and another two small peaks at 30 Hz (denoted as low-frequency arc in the figure, L) and 2 Hz. In comparison, the DRT analysis of YL1000 shows three peaks at 2 Hz, 10 Hz and 2×10^2 Hz (denoted as low-frequency arc in the figure, L) and an additional high-frequency arc at 2×10^3 Hz (denoted as high-frequency arc in the figure, H). As introduced in the Experimental section, the process at a frequency around 10^3 Hz is related to charge transfer (electron and oxygen ion transfer) process, the process with a frequency around 10^2 Hz represents the mass transfer (oxygen adsorption/desorption, dissociation/association and diffusion) process and the process around 10 Hz is associated with gas diffusion (A. Leonide et al., 2008; Schichlein et al., 2002).

From Figure VII-1c one can see that after the first 30 min of the electrolysis test of YL1000, low-frequency peak shrank and high-frequency arc disappeared with the emergence of a medium-frequency peak. After that, low-frequency peak increased again and gradually medium-frequency peak diminished and merged into the low-frequency peak. For YL800 in Figure VII-2c, during the initial 30 min test, medium-frequency peak shrank to a less extent compared with YL1000. Then, another low-frequency peak, L', emerged, which corresponds to the degradation afterwards as shown in Figure VII-2b. The mechanism of this degradation will be carefully studied in the near future.

In addition, to investigate the behaviours of the processes of different frequencies of YL1000, polarization resistances of different frequencies tested under different temperatures were obtained by curve fitting and the evolution of activation energy was also calculated. It can be observed in Figure VII-1 that the EIS curves tested at 800 °C suffer from severe distortion after electrolysis current passage especially at low-frequency end. This is a result of the recovery of the LSCF electrode to its original state from the changes caused by the electrolysis current. The distortion is too obvious compared with the small

impedance curves obtained at 800 °C, leading to inaccuracies during curve fitting and thus these curves were excluded. EIS curves tested at 750 °C is used to show the evolution of resistances of different frequencies.

Firstly, DRT analysis was conducted to obtain peak information as shown in Figure VII-4. It can be observed that YL1000 presented three peaks when the testing temperature was equal to or below 750 °C while for the rest samples, only medium- and low-frequency arcs can be observed. To make the comparison straightforward, the high- and low-frequency processes in YL1000 were fitted by only one arc and denoted as medium-frequency arc. Thus, the equivalent circuit used in this part is $LR_S(CPE_M R_{P,M})(CPE_L R_{P,L})$. All the fitting parameters can be found in Table VII-1.

Figure VII-4 DRT analysis of YL1000 (Half-cells with LSCF electrodes sintered on YSZ electrolytes at 1000 °C) tested at different temperatures (a) at the beginning of the test and after (b) 30 min, (c) 60 min and (d) 120 min electrolysis test.

Table VII-1 Fitting parameters of YL1000 (Half-cells with LSCF electrodes sintered on YSZ electrolytes at 1000 °C) for the first 2 h of electrolysis test under 1 A cm⁻² at 800 °C

Time/ min	Testing Temperature/ °C	Medium-Frequency Arc			Low Frequency Arc		
		$R_{P,M}/$ $\Omega \text{ cm}^2$	$Y_{0,M}/$ $\Omega^{-1} \text{ cm}^{-2} \text{ s}^{-n}$	n_M	$R_{P,L}/$ $\Omega \text{ cm}^2$	$Y_{0,L}/$ $\Omega^{-1} \text{ cm}^{-2} \text{ s}^{-n}$	n_L
0	775	0.58	5.52×10^{-3}	0.70	1.53	4.11×10^{-3}	0.89
	750	0.90	4.31×10^{-3}	0.71	2.58	3.72×10^{-3}	0.89
	725	1.42	3.40×10^{-3}	0.71	4.46	3.38×10^{-3}	0.88
	700	2.27	2.77×10^{-3}	0.72	8.01	3.05×10^{-3}	0.87
30	775	0.19	5.48×10^{-3}	0.86	0.90	4.99×10^{-3}	0.91
	750	0.30	5.16×10^{-3}	0.85	1.51	4.34×10^{-3}	0.91
	725	0.50	5.10×10^{-3}	0.84	2.47	3.92×10^{-3}	0.92
	700	0.79	4.77×10^{-3}	0.84	4.16	3.57×10^{-3}	0.92
60	775	0.09	4.40×10^{-3}	1.06	1.03	4.80×10^{-3}	0.92
	750	0.16	2.94×10^{-3}	1.00	1.66	4.36×10^{-3}	0.93
	725	0.25	3.19×10^{-3}	0.99	2.68	4.06×10^{-3}	0.93
	700	0.40	3.43×10^{-3}	0.98	4.43	3.81×10^{-3}	0.93
120	775	0.07	2.48×10^{-3}	1.06	0.90	5.53×10^{-3}	0.93
	750	0.12	3.06×10^{-3}	1.02	1.45	5.12×10^{-3}	0.94
	725	0.20	4.03×10^{-3}	0.99	2.35	4.93×10^{-3}	0.94
	700	0.33	4.42×10^{-3}	0.97	3.88	4.81×10^{-3}	0.94

The evolution of medium- and low-frequency polarization resistances tested under OCV at 750 °C is shown in Figure VII-5a. During the initial 120 min of the electrolysis test, decrease of both $R_{P,M}$ and $R_{P,L}$ can be observed, indicating an improvement on both mass transfer and charge transfer processes. Evolution of activation energy of YL1000 is shown in Figure VII-5b. During the electrolysis test, the activation energy of the total impedance decreased. In details, the activation energy of medium-frequency arc increased and the activation energy of the low-frequency arc decreased. The change of activation energy suggests that changes of materials properties have taken place during the electrolysis test.

Figure VII-5 (a) Evolution of medium- ($R_{P,M}$) and low-frequency ($R_{P,L}$) polarization resistance and total polarization resistance ($R_{P,Total}$) of YL1000 (Half-cells with LSCF electrodes sintered on YSZ electrolytes at 1000 °C) obtained by fitting EIS curves obtained at 750 °C under OCV; (b) Evolution of medium-arc , low-arc and total activation energy of YL1000 during the first 2 h of the electrolysis test under 1 A cm⁻² at 800 °C

7.4 Characterization of the Electrode–Electrolyte Interfaces

The characterization of the electrode–electrolyte interfaces was conducted by examining the surface of the YSZ electrolyte where it was in contact with the LSCF electrode. The LSCF electrodes were removed using diluted nitric acid except for YL1000 after the test, of which the YSZ electrolyte was observed directly since the LSCF electrode has entirely delaminated.

Figure VII-6 shows the FESEM images of the cross-section of YL1000 and YSZ electrolyte surfaces before the polarization test. EDX examinations were conducted on the areas indicated in the images and the results are shown in the insets as well as listed in Table VII-2. Figure VII-6a is the cross-section of YL1000. As indicated by the red rectangle, a thin layer of ~100 nm in thickness can be observed in between the LSCF electrode and the YSZ electrolyte. The electrolyte surfaces of YL1000, YL800 and bare electrolyte are shown in Figure VII-6b, Figure VII-6c, and Figure VII-6d, respectively. The morphologies were analysed before in Chapter IV and will not be repeated here.

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EDX analysis was performed on YL1000 and shows that the cations of the surface substance in Figure VII-6b are Zr (25 at. %) and Sr (12 at. %) with trace La (4 at. %). The other elements in the LSCF phase such as Co and Fe were not detected. Hence, it can be inferred that the observed layer in Figure VII-6a and the surface in Figure VII-6b is the inter-diffusion layer between the LSCF electrode and the YSZ electrolyte developed during the sintering process.

Figure VII-6 FESEM images and EDX results of YL1000 (Half-cells with LSCF electrodes sintered on YSZ electrolytes at 1000 °C) and YL800 (Half-cells with LSCF electrodes sintered on YSZ electrolytes at 800 °C) before the test. (a) Cross-section of YL1000; (b) surface of YSZ electrolyte of YL1000 and (c) of YL800 after the removal of the LSCF electrode; (d) bare YSZ electrolyte surface. The yellow rectangle indicates the area of EDX examination.

Table VII-2 Results of EDX examinations of the electrolyte surfaces of YL1000 (Half-cells with LSCF electrodes sintered on YSZ electrolytes at 1000 °C), including freshly-prepared sample and samples after electrolysis test for different periods (0.5 h, 12 h and 24 h) under 1 A cm⁻² at 800 °C

		La	Sr	Co	Fe	Zr	O
Freshly-prepared Sample (at. %) ¹		4	12			25	58
After 0.5 h Electrolysis test (at. %) ¹	C1 ³	3	12	14	3	16	52
	C2	4	17	6	2	21	50
	C3	5	17	9	2	20	47
	C4	3	14	6	2	17	58
	C Average	4	15	8	2	19	52
	D	2	13	2	4	17	62
After 12 h Electrolysis test (at. %) ²	E1			11		23	66
	E2			9		28	63
	E3			13		22	65
	E4			7		26	67
	F1			2		37	61
	F2			3		29	68
	F3			3		38	59
	F4			3		31	66
	E Average			10		25	65
	F Average			3		34	63
	G			5		28	67
After 24 h Electrolysis test (at. %) ²	A	4	16	3		20	57
	B			5		30	65

1: The LSCF electrodes of these two samples were removed by ultrasound treatment in diluted nitric acid for 30 min.

2: The electrolyte surfaces of these two samples were observed directly as LSCF electrodes has partially or completely delaminated from the electrolyte.

3: Capital letters indicate the places where the EDX examinations were performed, which are also indicated in Figure VII-6b, Figure VII-8b, Figure VII-8c, Figure VII-8b and Figure VII-9c. C, E and F are point-scans while A, B, D and G are area-scans.

XRD examinations were conducted again and XRD patterns of the electrolyte surfaces before the test of YL1000 and YL800 are shown in Figure VII-7a and Figure VII-7b, respectively. The patterns are consistent with the study in Chapter IV and confirm that the inter-diffusion layer is composed of

SrZrO₃ layer. Also, it is worth mentioning again that the inter-diffusion layer of YL1000 covers the whole surface of the YSZ electrolyte.

Figure VII-7 XRD patterns of the YSZ surface after the removal of the LSCF electrode. (a) YL1000 (Half-cells with LSCF electrodes sintered on YSZ electrolytes at 1000 °C) before the electrolysis test; (b) YL800 (Half-cells with LSCF electrodes sintered on YSZ electrolytes at 800 °C) before the electrolysis test; (c) YL1000 after the electrolysis test.

To investigate the cause for the electrochemical behaviour of YL1000, the YSZ surface after the delamination of the electrode was examined by SEM and the images are shown in Figure VII-8. In Figure VII-8a, two different morphologies are spotted and indicated by A and B. Figure VII-8b and c show the enlarged images of point A and B, respectively. According to the EDX analysis, the cations at point A are Zr (20 at. %), Sr (16 at. %), La (4 at. %) and

Co (3 at. %). Except for Co, the rest cations are identical to those contained in the SrZrO_3 layer observed in Figure VII-6b, suggesting that the substance from point A is the residue of the layer. In comparison, point B is free of any other cations in LSCF except for some Co (5 at. %) and mainly consists of Zr (30 at. %), indicating that this layer is the pure YSZ surface. This observation reveals that the SrZrO_3 layer delaminated from the YSZ electrolyte surface during the test rather than that the LSCF electrode delaminated from the SrZrO_3 layer. The emergence of Co could come from the diffusion of Co from the LSCF electrode.

XRD examination of the YSZ surface of YL1000 after the test was also conducted and the pattern is shown in Figure VII-7c, which is similar to that before the test. Peak integration was performed for the YSZ peak at $2\theta \approx 30^\circ$ and the SrZrO_3 peak at $2\theta \approx 31^\circ$ to render a semi-quantitative comparison. The results are illustrated in Figure VII-7. The relative content of SrZrO_3 to YSZ fell from 10% before the test to 4% after the test, which corresponds to the residues shown in Figure VII-8b. This again proves that the SrZrO_3 layer has delaminated. However, although EDX analysis confirms the existence of Co, no peak corresponding to any simple Co oxides were detected. Thus, it is possible that a solid solution has formed.

Figure VII-8 (a) An overview FESEM image of the YSZ electrolyte surface of YL1000 (Half-cells with LSCF electrodes sintered on YSZ electrolytes at 1000 °C) after the electrolysis test under 1 A cm⁻² for 24 h at 800 °C; (b) An enlarged image of point A in Figure VII-8a; (c) An enlarged image of point B in Figure VII-8a. The yellow rectangles indicate the area of EDX examination.

To further understand the process of the morphological and compositional changes of the electrode–electrolyte interface, two more samples of YL1000 were tested under an electrolysis current of 1 A cm⁻² at 800 °C for 0.5 h and 12 h, respectively. It was observed that the LSCF electrode was still well adhered to the electrolyte after 0.5 h polarization, while the LSCF electrode delaminated partially after 12 h polarization. The electrolyte surfaces of these two samples are shown in Figure VII-9 (Figure VII-9b and Figure VII-9c). For the sample after 0.5 h test, the LSCF electrode was removed by acid washing and for the sample after 12 h test, the part of the electrolyte where the LSCF has

delaminated was observed. The electrolyte surfaces of freshly prepared sample (Figure VII-9a) and the samples tested for 24 h (Figure VII-9d) are shown together for easy comparison. EDX examinations were also performed on different parts of the surfaces as marked in Figure VII-9 by capital letters and rectangles and the results are summarized in Table VII-2.

Comparing Figure VII-9a with Figure VII-9b, one can see that after 0.5 h electrolysis test, the surface of the SrZrO_3 layer of YL1000 was roughened and the grains of SrZrO_3 phase are distinguishable. Besides the morphological changes, the composition has also changed. By EDX, additional 2 at. % Co was detected on area D compared with the sample before the test. Moreover, some stick-like residues can be observed at the grain boundaries as indicated with symbols, C1 to C4, in Figure VII-9b. EDX analysis shows higher Co content with an average of 8 at. %, at these places. This finding demonstrates that Co diffusion from the LSCF electrode to the SrZrO_3 layer has already happened after the first 0.5 h polarization test. Correspondingly, fast activation was observed as shown in region I in Figure VII-1b, which may be related to the Co diffusion.

In Figure VII-9c, the YSZ surface of YL1000 after 12 h electrolysis test is found to be partially covered with small particles with an average diameter of ~60 nm. EDX area analysis (G) shows that Co content is 5 at. %, together with 28 at. % Zr. EDX point-analysis reveals that average Co content is 10 at. % on the particles (E1 to E4), higher than 3 at. % on the places without particles (F1 to F4). Thus, the particles on the YSZ surface is possibly originated from Co diffusion. Moreover, a nitric acid washed sample was also examined by EDX and has a composition of 6 at. % Co and 31 at. % Zr. Thus, the surface Co is

most likely to be Co in YSZ lattice, which is in accordance with the XRD analysis, as simple Co oxides are easily dissolved into nitric acid.

Figure VII-9 FESEM images of the surfaces of the YSZ electrolytes of YL1000 (Half-cells with LSCF electrodes sintered on YSZ electrolytes at 1000 °C) (a) before and (b-d) after the electrolysis test under 1 A cm^{-2} at 800 °C for different periods: (b) 0.5 h, (c) 12 h and (d) 24 h.

In Figure VII-9d, the YSZ surface of YL1000 after 24 h electrolysis test is fully covered by the small particles with an average diameter of ~50 nm. Comparing Figure VII-9d with Figure VII-9c, although the Co contents are equal (5 at. %), a spread of Co-based particles can be recognized from some parts of the YSZ surface to the whole surface. To sum up, in region II and III of the high-current electrolysis test shown in Figure VII-1b, the variation of R_p is accompanied by the Co diffusion to the YSZ surface. Yet at the same time, the delamination process is also progressing, weakening the contact between the electrode and the electrolyte. Thus, the first-decrease-and-then-increase behaviour of R_p is most likely a result of the trade-off between the Co diffusion and the delamination.

Mutual diffusion of LSCF electrode and the adjacent electrolyte has been observed previously (Laurencin et al., 2017; Z. P. Li et al., 2011). Especially, Laurencin *et al.* (Laurencin et al., 2017) has reported Co diffusion into the GDC interlayer after electrolysis test under 0.5 A cm^{-2} at 850°C for 1500 h. Also, they cannot detect any Co oxide phase by XRD. This could be the result of either the formation of a solid solution or the particle of Co phase was too small to be detected. By EDX mapping, the authors discussed that the Co should exist as a separate phase rather than merging into the lattice of GDC, as the distribution of Co did not overlap with Ce. By STEM-EDX, the authors inferred that the Co segregates could be Co–Fe oxides. Nonetheless, the exact composition and existing phase of the diffused Co is still unclear and needs further investigation.

7.5 Effect of Co Diffusion on YL1000 (Half-Cells with LSCF Electrodes Sintered on YSZ Electrolytes at 1000 °C)

In the above two sections, the improvement of the performance of YL1000 by 1 A cm^{-2} electrolysis current was observed being accompanied by Co diffusion. However, it is hard to conclude at this moment that the Co diffusion is the cause for the activation of the electrode. Thus, the following experiment was conducted to understand the effect of the Co diffusion on the electrochemical performance. A YL1000 was firstly tested at 800 °C for 24 h with an electrolysis current of 1 A cm^{-2} , during which Co should have diffused into the YSZ electrolyte. After cooling down, the LSCF electrode was found to have delaminated from the electrolyte, which agrees with the above observations. After that, the surface of the YSZ electrolyte substrate from which the LSCF electrode has delaminated was washed by nitric acid and then re-applied with LSCF slurry followed by sintering at the same temperature of 1000 °C. At last, EIS test and electrolysis test was performed again on the sample.

The YSZ electrolyte surface after the removal of the re-applied LSCF electrode by acid washing was also characterized as shown in Figure VII-10a. Firstly, EDX analysis of the surface confirms the existence of 7 at. % Co on the YSZ surface, which is much higher than its stoichiometric value. In contrast, no Co was detected on the newly prepared sample (Figure VII-6b). Secondly, the XRD pattern shown in the inset of Figure VII-10a confirms the formation of 11% SrZrO_3 second phase relative to YSZ phase. This value is higher than the 4% SrZrO_3 after the 24 h electrolysis test (Figure VII-7c), demonstrating that SrZrO_3 second phase has again formed during the second sintering process.

Therefore, by this way, the Co diffused to the YSZ electrolyte during the previous 24 h electrolysis test was included in the LSCF–YSZ interface after the re-application of LSCF electrode and a Co-containing SrZrO₃ layer has formed, which can be used to study the effect of Co diffusion.

Figure VII-10b shows the evolution of R_P of the newly prepared LSCF electrode and re-applied LSCF electrode. For the first 24 h, the change of R_P of the newly prepared LSCF electrode followed the same first-decrease-and-then-increase trend as in Figure VII-1b. After that, the re-applied LSCF electrode showed an initial R_P of $0.99 \Omega \text{ cm}^2$, which is much smaller than the initial R_P of the newly prepared LSCF electrode, $2.43 \Omega \text{ cm}^2$. Another 24 h electrolysis test was also conducted on the re-applied LSCF electrode. A similar activation step for the re-applied LSCF electrode can be observed but to a less extent compared with the freshly prepared one. Specifically, during the first 1 h of the electrolysis test, R_P decreased from 2.43 to $0.80 \Omega \text{ cm}^2$ (Decrease by 67%) for the freshly prepared LSCF electrode, while R_P decreased from 0.99 to $0.62 \Omega \text{ cm}^2$ (Decrease by 37%) for the re-applied LSCF electrode. Above results demonstrate that the existing Co substance in the SrZrO₃ layer can both improve the electrode performance and diminish the activation effect during the test on the re-applied LSCF electrode. This indicates that the improvement by the electrolysis current is caused by the Co diffusion. Furthermore, Co diffusion could alter the materials properties, which is in agreement with the changes of activation energy during the electrolysis test as analysed above.

Figure VII-10(a) SEM image of the YSZ electrolyte surface after the removal of the re-applied LSCF electrode sintered at 1000 °C by acid washing (XRD pattern and EDX analysis of the surface are shown in the insets); **(b)** Evolution of R_p for newly prepared YL1000 during the 24 h electrolysis test with an anodic current of 1 A cm⁻² at 800 °C and evolution of R_p for the re-applied LSCF electrode for another electrolysis test under the same condition

7.6 Discussion

The reaction between LSCF and YSZ, when sintered together at high temperature, forming SrZrO₃ second phase together with the precipitation of

spinel phase, has been presented in Chapter IV. The formation of the second phase was proven to have serious negative effect on the electrochemical performance of the LSCF electrode, because SrZrO_3 phase is an insulation in nature. The total conductivity is less than $10^{-3} \text{ S cm}^{-1}$ at 800°C and the oxygen ion transference number varies from 0.2 to 1 (Huang et al., 1995). In this part, a thin layer of SrZrO_3 with a thickness of $\sim 100 \text{ nm}$ was again observed covering the whole YSZ electrolyte surface, leading to the poor conduction of both oxygen species and electrons. Thus, the initial R_P is much larger for YL1000, $1.53 \Omega \text{ cm}^2$, than YL800, $0.14 \Omega \text{ cm}^2$ (Figure VII-1 and Figure VII-2).

On the other hand, the activation of R_P during the electrolysis test was evidenced, which was accompanied by Co diffusion as confirmed by EDX analysis. In Figure VII-10b, the inclusion of Co in the SrZrO_3 layer was shown to have a positive influence on the electrochemical performance of the LSCF electrode and diminish the activation process. This can be attributed to the positive impact of Co on the catalytic activity as reported in the previous literature (D. Chen et al., 2011; J. Druce et al., 2013; Kan & Wachsman, 2009; Takeda et al., 1987). In perovskite phase, Co element was found to be a catalytically active element towards the oxygen reduction reaction (Takeda et al., 1987). Kan and Wachsman (Kan & Wachsman, 2009) conducted a systematic surface modification of LSM electrode with various metal nitrate solutions (La, Sr, Co and Fe). The results showed that Co infiltration could improve the performance. Druce and Kilner (J. Druce & Kilner, 2013) has modified the surface of GDC electrolyte with Co nitrate solutions and this turned out to be positive in facilitating the surface exchange process. In a full cell, Chen et al. (D. Chen et al., 2011) has proven that the addition of Co_3O_4

into BSCF cathode could lower the R_p and increase the peak power density. Consequently, the decrease of R_p of YL1000 during the electrolysis test could be a result of Co diffusion.

Derived from above findings and analysis, a detailed activation and delamination process of YL1000 is schematically shown in Figure VII-11. In Figure VII-11a, a thin but dense layer of SrZrO_3 second phase forms at the electrode–electrolyte interface (shown in Figure VII-6b) of a freshly prepared sample, as a result of the high sintering temperature of 1000 °C. In Figure VII-11b, after the first 0.5 h electrolysis test at 1 A cm^{-2} , Co diffuses to the SrZrO_3 layer and the surface of the SrZrO_3 layer roughens, increasing the electrochemical activity of the SrZrO_3 layer. This leads to a substantial decrease of R_p . After that in Figure VII-11c, the improved catalytic activity by Co-diffusion to the SrZrO_3 layer renders the generation of oxygen at the SrZrO_3 –YSZ interface during the electrolysis test. However, the oxygen molecules generated cannot efficiently diffuse away to the atmosphere, due to the low porosity of the SrZrO_3 layer. Thus, the accumulated oxygen gradually weakens the bonding between the SrZrO_3 layer and the YSZ electrolyte. In Figure VII-11d, the electrode has partially delaminated and Co-phase emerges on the YSZ electrolyte (Figure VII-9c) after 12 h test. Eventually (Figure VII-11e), high oxygen partial pressure causes the complete delamination at the SrZrO_3 –YSZ interface except for some local residues of SrZrO_3 as shown in Figure VII-8b, resulting in the increase of R_p and R_s . Besides, the surface of the exposed YSZ electrolyte is fully covered with Co-based substance (Figure VII-9d). However, the exact composition and phase of the Co-based substance is still unclear, which will be investigated in the future.

Figure VII-11 Schematic of the mechanism for the activation and delamination of LSCF air electrode of YL1000 (Half-cells with LSCF electrodes sintered on YSZ electrolytes at 1000 °C). (a) Freshly prepared sample; (b) Sample after 0.5 h high-current electrolysis; (c) Sample during the high-current electrolysis test; (d) Sample after 12 h electrolysis test; (e) Sample after 24 h electrolysis test.

Above mechanism is also supported by the test on YL800. Due to the much lower sintering temperature, no detectable SrZrO_3 second phase formed during the sintering process. Within the testing period of 24 h, delamination phenomenon was not observed on YL800 as shown in Figure VII-3b. Therefore, the formation of the SrZrO_3 layer during the sintering process has an effect on the stability of the LSCF electrode sintered at 1000 °C. Even though it is not the sole reason for the delamination, the SrZrO_3 layer at least accelerates the delamination process.

From another perspective, even that it is found that the formation of SrZrO_3 second phase could lead to delamination of the LSCF electrode, the essential reason is still the high oxygen partial pressure that builds up at the SrZrO_3 –YSZ interface. This is consistent with the modelling work done by Virkar (Anil V. Virkar, 2010). However, in other studies on the delamination mechanisms of LSM-based electrodes, structural changes were observed. For instance, disintegration of LSM particles into nanoparticles were observed by Chen et al. (K. Chen & Jiang, 2011) and formation of $\text{La}_2\text{Zr}_2\text{O}_7$ nanoparticles was observed by Keane et al. (Keane et al., 2012). In addition, in this work, how the delamination starts and propagates is still not clear. Further studies are needed to clarify it.

In addition, the delamination phenomenon is universally observed even when a GDC interlayer is employed to prevent the interfacial reaction between LSCF and YSZ (Fan, Keane, Singh, et al., 2014; Hjalmarsson et al., 2013; Kim & Choi, 2014). The mechanism proposed in this work could also provide an explanation on this phenomenon. Previous report has shown that SrZrO_3 can form locally at the YSZ–GDC interface when the GDC layer was fabricated by

PLD (Knibbe, Hjelm, et al., 2010). Even if there is no formation of SrZrO_3 second phase for freshly prepared cell with GDC interlayer, the electrolysis current can facilitate the diffusion of Sr and Zr during the polarization and thus the formation of SrZrO_3 (F. Wang, M. E. Brito, et al., 2014; F. Wang, M. Nishi, et al., 2014). Post-mortem analysis after the electrolysis test also revealed the formation of the SrZrO_3 phase at the GDC–YSZ interface (Tietz et al., 2013). After the formation of SrZrO_3 second phase, delamination could proceed following the proposed mechanism. The proposed activation and failure mechanism implies that the prevention of SrZrO_3 formation and Co diffusion during the electrolysis operation is important to prevent the delamination of LSCF air electrode.

7.7 Conclusion

In this part, the mechanism for the activation and the subsequent delamination of the LSCF electrode sintered on YSZ electrolyte at 1000 °C in SOEC was investigated. During the electrolysis test at 1 A cm^{-2} at 800 °C for 24 h, R_P showed an initial decrease in the first 18 h and then increased again. At the same time, R_S was relatively stable in the first 18 h followed by an abrupt increase in the last 6 hours. In addition, the initial improvement on the performance was accompanied by changes in the activation energy. The characterization of the YSZ surface after the removal of the LSCF electrode showed that a thin but dense SrZrO_3 layer has formed at the LSCF–YSZ interface of a freshly prepared sample, which caused the high R_P of Y1000. After the electrolysis test, it is the SrZrO_3 layer delaminated from the YSZ electrolyte rather than the LSCF electrode delaminated from the SrZrO_3 layer. EDX analysis confirmed the diffusion of Co into the SrZrO_3 layer and the YSZ

electrolyte. Later, the LSCF electrode with Co-containing SrZrO_3 layer was shown to possess better electrochemical performance and less activation process under electrolysis current than the LSCF electrode with pure SrZrO_3 layer. Thus, Co diffusion is most likely the reason for the activation phenomenon, which agrees with the changes in activation energy, and renders the generation of oxygen molecules at the SrZrO_3 –YSZ interface. However, the oxygen generated cannot diffuse out efficiently due to the low porosity of the SrZrO_3 layer. Eventually, high oxygen partial pressure built up and weakened the bonding and caused the delamination of the SrZrO_3 layer. The proposed activation and failure mechanism can also provide an explanation on the delamination phenomenon when a GDC interlayer is used. As SrZrO_3 may develop at some places during the long-term operation, local delamination may take place following the same process but taking longer time.

Chapter VIII Short-Term Stability Tests of LSCF Air Electrodes

8.1 Introduction

In Chapter VII, it was found that the formation of SrZrO_3 at the LSCF–YSZ interface would cause severe delamination problem during the high-current electrolysis. To prevent the formation of SrZrO_3 , fully dense GDC interlayer is needed or the sintering temperature of LSCF electrodes should not be higher than 800 °C as revealed by the XRD results shown in Chapter IV. In this chapter, short-term electrolysis tests under high electrolysis current of 1 A cm^{-2} at 800 °C for extended duration, up to 264 h, were conducted on half-cells with 6 different configurations. The effectiveness of sintering LSCF electrodes at 800 °C and the use of a dense GDC interlayer in preventing the delamination problem can be examined. In addition, by comparing the performance of half-cells with different configurations, the effect of the air electrode–electrolyte interface on the short-term stability of LSCF electrodes can be better understood. At the end, the most durable cell will be identified as a baseline cell for future test and improvement.

8.2 Experimental Details

Short-term stability tests were conducted on half-cells with 6 different configurations of different electrolytes, different air electrodes, and different sintering temperatures. Therefore, the optimal cell configuration for future test can be identified. The electrolytes used are YSZ electrolyte, GDC electrolyte, YSZ electrolyte with porous GDC interlayer or YSZ electrolyte with dense

GDC interlayer. The sintering temperatures of LSCF electrodes were chosen to be 800 or 1000 °C. In addition, half-cells with Pt electrodes were also fabricated to investigate the degradation from the electrolyte during electrolysis test. Details of the 6 samples are summarized in Table VIII-1.

Table VIII-1 Fabrication conditions of the half-cells for the short-term test under 1 A cm⁻² electrolysis current at 800 °C

Sample	Electrolyte	GDC interlayer	Air electrode	Sintering temperature of air electrode(°C)
YL800	YSZ	Nil	LSCF	800
YL1000	YSZ	Nil	LSCF	1000
GL1000	GDC	Nil	LSCF	1000
YGpL1000	YSZ	Porous (by spin coating and sintering at 1200 °C)	LSCF	1000
YGdL1000	YSZ	Dense (by spraying and co-sintering with YSZ at 1400 °C)	LSCF	1000
YPt1000	YSZ	Nil	Pt	1000

8.3 Results of Short-Term Stability Tests

Half-cells with six different configurations were tested under an electrolysis current of 1 A cm⁻² at 800 °C for 264 h (288 h for YL800 and 36 h for YL1000). The evolution of Nyquist plots are presented in Figure VIII-1a to Figure VIII-6a. It should be pointed out that direct comparison of the R_p between different samples is possible and will be discussed subsequently. However, direct comparison of the R_s will not be made due to the fact that

many factors are attributing to this value. The changes of R_P and R_S during the test for different samples were extracted and plotted in Figure VIII-1b to Figure VIII-6b. For YL1000 of which the results are shown in Figure VIII-2, the electrolysis test was stopped due to an abrupt increase of R_P and R_S from 24 h to 36 h. After unloading the cell, it was found that the LSCF electrode completely delaminated, which could be the reason for the abrupt increase in R_P and R_S , in good agreement with the test result shown in Chapter VII.

In addition, at the beginning of the test, there are some fluctuations or activation–deactivation processes. Thus, to gain a better understanding on the stability of the LSCF electrodes, the degradation rate was calculated based on the data from 0 to 96 h and 96 h to 264 h (288 h for YL800), respectively, and the latter period will be mainly discussed. Table VIII-2 summarizes the results of the electrolysis test including the resistances at the beginning of each period, the degradation rates, the formation of SrZrO_3 second phase, and delamination problem. In the following parts, detailed discussion is to be made to understand the effect of the air electrode–electrolyte interface on the stability.

Figure VIII-1 Evolution of (a) Nyquist plots and (b) resistances of YL800 (Half-cells with LSCF electrodes sintered on YSZ electrolytes at 800 °C) during electrolysis test under 1 A cm⁻² for 288 h at 800 °C

Figure VIII-2 Evolution of (a) Nyquist plots and (b) resistances of YL1000 (Half-cells with LSCF electrodes sintered on YSZ electrolytes at 1000 °C) during electrolysis test under 1 A cm⁻² for 36 h at 800 °C

Figure VIII-3 Evolution of (a) Nyquist plots and (b) resistances of GL1000 (Half-cells with LSCF electrodes sintered on GDC electrolytes at 1000 °C) during electrolysis test under 1 A cm⁻² for 264 h at 800 °C

Figure VIII-4 Evolution of (a) Nyquist plots and (b) resistances of YGpL1000 (Half-cells with YSZ electrolytes, porous GDC interlayers and LSCF electrodes sintered at 1000 °C) during electrolysis test under 1 A cm⁻² for 264 h at 800 °C

Figure VIII-5 Evolution of (a) Nyquist plots and (b) resistances of YGdL1000 (Half-cells with YSZ electrolytes, dense GDC interlayers and LSCF electrodes sintered at 1000 °C) during electrolysis test under 1 A cm⁻² for 264 h at 800 °C

Figure VIII-6 Evolution of (a) Nyquist plots and (b) resistances of YPt1000 (Half-cells with Pt electrodes sintered on YSZ electrolytes at 800 °C) during electrolysis test under 1 A cm⁻² for 264 h at 800 °C

Table VIII-2 Results for the six samples after electrolysis test under 1 A cm^{-2} at 800°C for 264 (288 h for YL800 and 36 h for YL1000)

Sample	SrZrO ₃	<i>R</i> at <i>t</i> = 0 h		Degradation rate (0 – 96 h)*		<i>R</i> at <i>t</i> = 96 h		Degradation rate (96 – 264 h)**		Delamination after test?
	formation	(Ω cm ²)		(Ω cm ² /100 h – %/100 h)		(Ω cm ²)		(Ω cm ² /100 h – %/100 h***)		
	before test?	<i>R</i> _P	<i>R</i> _S	<i>R</i> _P	<i>R</i> _S	<i>R</i> _P	<i>R</i> _S	<i>R</i> _P	<i>R</i> _S	
YL800	No	0.036	1.7	0.34–946.3	0.066–3.8	0.36	1.8	0.21–58.0	0.14–7.8	No
YL1000	Yes	2.4	1.8	32–1325.9	32–1752.9	-	-	-	-	Yes
GL1000	No	0.040	0.51	0.025–62.7	0.10–20.0	0.064	0.60	0.069–108.2	0.022–3.6	No
YGpL1000	Yes	0.28	1.5	0.35–124.8	1.2–80.0	0.61	2.7	0.65–107.3	0.87–33.1	Yes
YGdL1000	No	0.042	1.1	0.034–80.9	0.19–16.8	0.074	1.3	0.035–47.1	0.061–4.6	No
YPt1000	No	0.39	0.97	0.81–208.3	0.17–17.2	1.17	1.13	–0.21– –17.6	0.054–4.7	No

*: For YL1000, the degradation rate was calculated based on the test from 0 h to 36 h due to severe delamination problem.

**: For YL800, the degradation rate was calculated based on the test from 96 h to 288 h.

***: Percentage was calculated based on the value obtained at 96 h except for YL1000.

8.4 Effect of the Air Electrode–Electrolyte Interface on the Initial Performance

At the beginning of the test, the order of R_P from low to high of the five samples with LSCF electrodes is $0.036 \, \Omega \, \text{cm}^2$ (YL800) $< 0.040 \, \Omega \, \text{cm}^2$ (GL1000) $< 0.042 \, \Omega \, \text{cm}^2$ (YGdL1000) $< 0.28 \, \Omega \, \text{cm}^2$ (YGpL1000) $< 2.4 \, \Omega \, \text{cm}^2$ (YL1000). Figure VIII-7 to Figure VIII-11 shows the SEM images of the samples before and after the test. EDX line scans were also performed on YL800, YL1000 and YGpL1000 and shown in the figures to study the formation of SrZrO_3 during the fabrication process. It can be seen that for YL1000 in Figure VIII-8a, aggregation of Sr at the LSCF–YSZ interface can be observed, which indicates the formation of SrZrO_3 and is the reason for the high R_P . As for YGpL1000, although a porous GDC interlayer of $1 \, \mu\text{m}$ has been added, the formation of SrZrO_3 was not totally prevented as reflected by the Sr aggregation in Figure VIII-10a. As a result, R_P of YGpL1000 is still higher than YL800, on which SrZrO_3 did not form. Moreover, it should be noted that the formation of SrZrO_3 in YGpL1000 is at the interface of GDC interlayer and YSZ electrolyte. This is most likely to be the result of Sr diffusion.

As for the rest three samples, YL800, GL1000 and YGdL1000, on which the SrZrO_3 did not form during the fabrication stage, the R_P is close to each other. This contradicts with previous report (M. Liu & Wu, 1998) and implies that the interfacial reaction must be considered when comparing the performance between YSZ and GDC electrolyte especially when tested at high temperatures. At last, R_P of YGdL1000 is similar to that of GL1000, indicating that the dense GDC interlayer shown in Figure VIII-11a can effectively prevent the formation of SrZrO_3 and function the same as a GDC electrolyte.

Figure VIII-7 Cross-section images of YL800 (Half-cells with LSCF electrodes sintered on YSZ electrolytes at 800 °C) (a) before and (b) after electrolysis test under 1 A cm⁻² for 288 h at 800 °C

Figure VIII-8 Cross-section images of YL1000 (Half-cells with LSCF electrodes sintered on YSZ electrolytes at 1000 °C) (a) before and (b) after electrolysis test under 1 A cm⁻² for 36 h at 800 °C

Figure VIII-9 Cross-section images of GL1000 (Half-cells with LSCF electrodes sintered on GDC electrolytes at 1000 °C) (a) before and (b) after electrolysis test under 1 A cm⁻² for 264 h at 800 °C

Figure VIII-10 Cross-section images of YGpL1000 (Half-cells with YSZ electrolytes, porous GDC interlayers and LSCF electrodes sintered at 1000 °C) (a) before and (b) after electrolysis test under 1 A cm⁻² for 264 h at 800 °C

Figure VIII-11 Cross-section images of YGdL1000 (Half-cells with YSZ electrolytes, dense GDC interlayers and LSCF electrodes sintered at 1000 °C) (a) before and (b) after electrolysis test under 1 A cm⁻² for 264 h at 800 °C

8.5 Effect of the Air Electrode–Electrolyte Interface on the Delamination Phenomenon

The cross-section images of the half-cells after the electrolysis tests were also obtained and shown in Figure VIII-7b to Figure VIII-11b. The electrodes of YL1000 and YGpL1000 were found to delaminate after the electrolysis test. Correspondingly, the degradation rates of these two samples are the two highest among the five samples. For YL1000, the degradation rate of R_p is 32 Ω

$\text{cm}^2/100 \text{ h}$ and of R_S is $32 \Omega \text{ cm}^2/100 \text{ h}$ during the 36 h test (After 36 h the test was stopped due to the delamination problem). For YGpL1000, the degradation rate of R_P is $0.65 \Omega \text{ cm}^2/100 \text{ h}$ and of R_S is $0.87 \Omega \text{ cm}^2/100 \text{ h}$ during 96–264 h. In comparison, degradation rates of the rest three samples during 96–264 h range from 0.035 to $0.21 \Omega \text{ cm}^2/100 \text{ h}$ for R_P and from 0.022 to $0.14 \Omega \text{ cm}^2/100 \text{ h}$ for R_S .

Furthermore, for YL1000 and YGpL1000 which show delamination problem, both of them had SrZrO_3 formation during the fabrication stage. This demonstrates a relation between the SrZrO_3 insulating phase formation and the delamination during high-current electrolysis. The mechanism underneath is associated with Co diffusion which causes oxygen accumulation at the SrZrO_3 –YSZ interface and hence the delamination of SrZrO_3 layer as studied Chapter VII. In this test, it can be again observed in Figure VIII-10b that the delamination took place at the SrZrO_3 –YSZ interface as signal of Sr and GDC layer cannot be detected by EDX line-scans.

The surface of the electrolyte after delamination and the inner surface of the detached electrode of YGpL1000 were also examined by SEM and EDX area-scans shown in Figure VIII-12. In Figure VIII-12a, existence of 5 at. % Co again proves Co diffusion. In Figure VIII-12b, 4 at. % Sr and 7 at. % Ce can be detected on the inner surface of the detached electrode, demonstrating that the SrZrO_3 phase and porous GDC interlayer has delaminated. These results support the conclusion made in Chapter VII that the formation of SrZrO_3 second phase could accelerate the delamination of LSCF air electrodes during high-current electrolysis.

Figure VIII-12 (a) YSZ surface after the delamination and (b) inner surface of the detached electrode of YGpL1000 (Half-cells with YSZ electrolytes, porous GDC interlayers and LSCF electrodes sintered at 1000 °C) after electrolysis test under 1 A cm⁻² for 264 h at 800 °C

Above analysis demonstrates that although the porous GDC interlayer used in YGpL1000 has improved the initial performance and reduced the degradation rate compared with YL1000, delamination eventually took place. One may argue that the porous GDC interlayer used here is rather thin, which leads to the formation of SrZrO₃, compared with a common one. However, after the 9000 h test done by Tietz et al. (Tietz et al., 2013), SrZrO₃ second phase still developed at GDC–YSZ interface even the GDC layer is 5 μm in thickness. After that, delamination might still have taken place following the same mechanism if the cell were to operate for 3 or 5 years, which is the expected lifespan for SOEC. Consequently, formation of SrZrO₃ should be strictly prevented and thus dense GDC interlayer is needed.

8.6 Effect of the Sintering Temperature of Electrode on the Short-Term Stability

By reducing the sintering temperature of LSCF electrodes on YSZ electrolytes, the formation of SrZrO₃ phase can also be prevented. From the EDX line-scan of YL800 in Figure VIII-7a, no aggregation of Sr at the interface

can be observed. As a result, no delamination appeared. However, the degradation rates during 96–216 h of YL800 are $0.21 \Omega \text{ cm}^2/100 \text{ h}$ for R_P and $0.14 \Omega \text{ cm}^2/100 \text{ h}$ for R_S . In contrast, the degradation rates during 96–216 h of GL1000 are $0.069 \Omega \text{ cm}^2/100 \text{ h}$ for R_P and $0.022 \Omega \text{ cm}^2/100 \text{ h}$ for R_S and of YGdL1000 are $0.035 \Omega \text{ cm}^2/100 \text{ h}$ for R_P and $0.061 \Omega \text{ cm}^2/100 \text{ h}$ for R_S . Although the three samples are all free from the formation of SrZrO_3 , the degradation rate of YL800 is two to three times of the other two samples. This could be a result of the low sintering temperature. During the test at 800°C , the LSCF electrode sintered at 800°C may suffer more severe particle agglomeration and particle size increase compared with the one sintered at 1000°C .

8.7 Ohmic Resistance Increase from Electrolyte

All the samples show increase in R_S during the electrolysis test. To locate the origin of this increase, from electrolyte or electrode, Pt was employed as air electrode and tested. The results are also shown in Figure VIII-6 and summarized in Table VIII-2. If one takes a close look at the rate of R_S increase during 96–216 h for YPt1000 and the most stable two samples with LSCF electrodes, i.e. GL1000 and YGdL1000, one can observe that although the rate of R_S increase in $\Omega \text{ cm}^2/100 \text{ h}$ is different for each sample, the percentage increase is rather close, 3.6%/100 h for GL1000, 4.6%/100 h for YGdL1000 and 4.7%/100 h for YPt1000. Firstly, this demonstrates that the degradation in R_S should not come from the LSCF electrode, since the half-cell with Pt electrode showed similar degradation. Secondly, the increase of R_S should come from structural changes like decrease of contact area or density of electrolyte which leads to a proportional increase. For instance, GDC electrolyte of

GL1000 after the test in Figure VIII-9b shows an area of 35 μm in width where GDC grains and grain boundaries are clearly distinguished, whereas this area is about 10 μm in width before the test, which may lead to a decrease in the contact area and an increase in ohmic resistance. Further detailed work needs to be conducted to study the mechanism and work out the solution.

8.8 Morphological Changes of LSCF Air Electrodes

Figure VIII-13 shows the morphology of the LSCF air electrode of GL1000 before and after the electrolysis test. Before the electrolysis test, the electrode is composed of round particles. However, after the test, the LSCF air electrode showed many more crystal faces and edges (Figure VIII-13b). This is in agreement with the LSCF electrode after 9000 h electrolysis (Tietz et al., 2013) and could be one of the reasons for the increase of R_p .

Figure VIII-13 Morphology of the LSCF air electrode of GL1000 (Half-cells with LSCF electrodes sintering on GDC electrolytes at 1000 °C) (a) before and (b) after the electrolysis test under 1 A cm⁻² for 264 h at 800 °C

8.9 Baseline Cell for Future Study

After the electrolysis test for all the cells with LSCF electrodes, a baseline cell for future study can be identified. For YL1000 and YGpL1000, they are excluded due to the delamination problem. For YL800, due to the instability

caused by the low sintering temperature of the LSCF electrode, the R_P at $t = 96$ h, the degradation rate of R_P and R_S during 96–264 h are all higher than these of YGd1000. Thus, YL800 can be ruled out. At last, due to the electronic leakage in GDC electrolyte, the Faradic efficiency will be lower than 100% and thus the efficiency of water electrolysis will be lower. Thus, pure GDC electrolyte is not suitable for SOEC. In addition, the dense GDC interlayer used in YGdL1000 can effectively function the same as GDC electrolyte in terms of the R_P at $t = 96$ h and degradation of R_P . The only problem of YGdL1000 is the high degradation rate in $\Omega \text{ cm}^2/100 \text{ h}$ of R_S , which needs to be further studied and suppressed. In summary, YGdL1000 is selected as the baseline cell for future study.

8.10 Conclusion

In this part, six different types of half-cells were tested to study the effect of air electrode–YSZ electrolyte interface on the short-term stability during high-current electrolysis under 1 A cm^{-2} at 800°C for 264 h. A few concluding remarks can be drawn by comparing the behaviours of different cells. Firstly, the delamination of air electrode had a relation with the formation of SrZrO_3 at the interface. Thus, the formation of SrZrO_3 should be strictly prevented. Secondly, increasing sintering temperature can decrease the degradation rate of R_P for LSCF electrodes. Thirdly, the increase of R_S comes from structural changes as the degradation rate in percentage is similar for different cells. However, mechanism underneath needs to be further studied. At last, comparing all the samples, YGdL1000 can be used for future study on the degradation mechanism of the LSCF air electrode and the electrolyte.

Chapter IX Conclusions and Recommendations

9.1 Conclusions

The objectives of this research are to characterize the application of LSCF as air electrodes in SOEC, to investigate the degradation phenomenon of LSCF air electrodes, and to develop methods to improve the stability. To this end, the formation of SrZrO_3 phase during the fabrication stage was firstly studied. Then, the mechanism for the degradation of LSCF electrodes during high-temperature anneal was deduced. Subsequently, the change of the electrochemical performance of LSCF air electrodes under electrolysis current was obtained. Particularly, during high-current electrolysis, the activation process at the beginning and the delamination of LSCF electrodes after the test were observed. Efforts were made to understand the mechanism for the activation and delamination behaviour. Finally, dense GDC interlayer was proposed in order to prevent the delamination of LSCF electrodes. In this work, the following concluding remarks are made:

1. The reaction between LSCF electrodes and YSZ electrolytes, forming a dense layer of SrZrO_3 second phase, is the main cause for the performance drop when the LSCF electrode is sintered at high temperature.

It was found that SrZrO_3 second phase started to form, along with the precipitation of $(\text{CoFe})_3\text{O}_4$ spinel phase, at a sintering temperature of 850 °C or higher when sintering LSCF and YSZ for 2 h. The polarization resistance of LSCF electrodes on YSZ electrolytes obtained under OCV increased from 0.03 $\Omega \text{ cm}^2$ to 2.72 $\Omega \text{ cm}^2$ with the sintering temperature increased from 800 °C to 1000 °C. By FESEM, a thin but dense layer of SrZrO_3 was observed covering the whole surface of the YSZ electrolyte

when the LSCF electrode was sintered at 1000 °C, most likely due to the high diffusivity of Sr. Furthermore, it was found that the SrZrO₃ second phase caused more severe performance drop in fuel cell mode than in electrolyzer mode.

2. The increase of the polarization resistance of LSCF electrodes during high-temperature anneal is related to the Sr surface segregation.

Three half-cells with LSCF air electrodes sintered on YSZ electrolytes at 900 °C were annealed under OCV for 24 h at different temperatures, 650 °C, 700 °C and 750 °C. With the increase of the testing temperature, the degradation rate increased. Moreover, the increase of polarization resistance during annealing test showed a linear dependence on the square root of time. ADIS analysis demonstrated that this increase mainly came from the change of process happening at around 100 Hz, which was previously identified as mass transfer process. A comparison of the behaviours of the sample before and after nitric acid etching treatment showed that the performance was improved and the degradation rate has been dramatically reduced after nitric acid etching treatment, indicating that the degradation is most likely due to the emergence of surface inhibiting species on the LSCF electrode, which can be removed by nitric acid. XPS examination showed that the “surface” Sr, including Sr²⁺ in the perovskite termination layer and Sr-based second phase like SrO, and/or the reaction products formed with chemi-absorbed gases (Sr(OH)₂·xH₂O and SrCO₃), increased upon the anneal and decreased upon the nitric acid etching treatment. In conclusion, the degradation of LSCF electrodes under OCV can be a result of surface segregation of Sr-based species,

which retards the mass transfer process, including oxygen surface adsorption/desorption, surface dissociation/association and surface diffusion.

3. The electrolysis current can stabilize or even activate the electrochemical performance of LSCF electrodes.

LSCF electrodes sintered at different temperatures on YSZ electrolytes, 800 °C (YL800), 900 °C (YL900), 950 °C (YL950) and 1000 °C (YL1000), were applied with an electrolysis current of 0.2 A cm⁻². It was found that for YL800 and YL900, the polarization resistance increased at first and then stabilized at a certain value; however for YL950 and YL1000, the performance was improved by the passage of the current and then stabilized. Furthermore, after the stabilization of YL900, increasing the current density could reduce the polarization resistance. Short-term test with alternate application of anodic current and open circuit on YL1000 again demonstrated that the polarization resistance decreased when the cell was applied with anodic current but increased during open circuit.

4. The activation of LSCF air electrodes arises from the Co diffusion into the SrZrO₃ layer during the electrolysis.

LSCF electrodes sintered on YSZ electrolytes at 1000 °C (YL1000) were tested under an electrolysis current of 1 A cm⁻² for 24 h at 800 °C. At the beginning of the test, a substantial decrease in polarization resistance was observed, from 1.53 Ω cm² to 0.59 Ω cm² within half an hour. FESEM images on the YSZ electrolyte surface after the removal of the LSCF electrode showed Co diffusion into the SrZrO₃ layer. To validate the effect of the Co diffusion, a YL1000 was firstly tested with a 1 A cm⁻²

electrolysis current for 24 h, during which Co could have diffused into the YSZ electrolyte and LSCF delaminated after the test. Then, LSCF electrode was again sintered on the YSZ electrolyte at 1000 °C and thus a YL1000 with Co-containing SrZrO₃ layer was fabricated. The YL1000 with Co-containing SrZrO₃ layer presented an initial polarization resistance of 0.99 Ω cm², which is much lower than that of the YL1000 with pure SrZrO₃ layer, 2.43 Ω cm². Furthermore, the polarization resistance of YL1000 with Co-containing SrZrO₃ layer decreased from 0.99 to 0.62 Ω cm² (decrease by 37%) while the polarization resistance of YL1000 with pure SrZrO₃ layer decreased from 2.43 to 0.80 Ω cm² (decrease by 67%) after 1 h electrolysis. Thus, the addition of Co into the SrZrO₃ layer can simultaneously improve the performance and diminish the activation process. This result indicates that the Co diffusion into the SrZrO₃ layer and the YSZ electrolyte could be the cause for the activation process during electrolysis test.

5. The delamination of LSCF air electrodes could be the result of the generation of oxygen at the SrZrO₃–YSZ interface, which leads to high oxygen partial pressure and weakens the bonding.

After the 24 h electrolysis test, the LSCF electrode was found to delaminate from the YSZ electrolyte. As revealed by FESEM images, the delamination was observed to take place at the SrZrO₃–YSZ interface, rather than the LSCF–SrZrO₃ interface. Due to the improved catalytic activity of the SrZrO₃ layer by Co diffusion as proved above, the oxygen may generate at the SrZrO₃–YSZ interface. However, the oxygen generated cannot diffuse out efficiently due to the low porosity of the

SrZrO₃ layer. Eventually, high oxygen partial pressure weakened the bonding and caused the delamination of the SrZrO₃ layer. The proposed activation and failure mechanism can also provide an explanation on the delamination phenomenon when a GDC interlayer is used. As SrZrO₃ may develop at some places during the long-term operation, local delamination may take place following the same process but taking longer time.

6. A half-cell with a dense GDC interlayer was subject to short-term electrolysis test under 1 A cm⁻² for 264 h at 800 °C and no delamination was observed.

No delamination phenomenon was observed after short-term electrolysis test when a dense GDC interlayer was added into a half-cell. By comparison, a porous GDC interlayer, which was later found to be unable to fully prevent the formation of SrZrO₃ second phase, was also fabricated and tested under the same condition. Detachment was again found at the interface between the SrZrO₃ phase and the YSZ electrolyte. In addition, the LSCF electrode sintered at 800 °C on the YSZ electrolyte was also tested. Although SrZrO₃ second phase did not form due to the low sintering temperature and thus no delamination occurred, the electrode suffered from severe performance degradation during the test. This result demonstrates the effectiveness of the addition of a dense GDC interlayer in preventing the delamination problem and achieving a better stability. Future work can be conducted on this configuration to investigate other degradation sources like phase change or Sr segregation.

9.2 Contributions and Achievements

Major contributions and achievement made in the project are summarized below:

1. The morphology of the SrZrO_3 second phase at the LSCF–YSZ interface was observed for the first time. When the LSCF electrode sintered at 1000 °C, the SrZrO_3 second phase was found to form a continuous dense layer covering the whole surface of the YSZ electrolyte, rather than forming only at where LSCF and YSZ are in contact. This thin but dense layer of SrZrO_3 was proven to cause significant performance drop of LSCF electrodes sintered at high temperatures.
2. The performance degradation of LSCF electrodes during high-temperature anneal was validated to be the result of the Sr surface segregation, confirming the detrimental role of surface segregated Sr on the electrochemical performance.
3. The mechanism for the activation and delamination of LSCF electrodes during high-current electrolysis was studied. The activation process could be related to the Co diffusion into the SrZrO_3 layer generated during the fabrication stage. Afterwards, due to the improved catalytic activity of the SrZrO_3 layer, oxygen could generate at the SrZrO_3 –YSZ interface and eventually led to the delamination of the SrZrO_3 layer.
4. Addition of a dense GDC interlayer between the YSZ electrolyte and the LSCF electrode in a half-cell is an effective way to prevent the delamination problem. After short-term electrolysis test under 1 A cm^{-2} for 264 h on the half-cell with a dense GDC interlayer, delamination of LSCF electrodes did not take place, while the cell with a porous GDC interlayer,

which cannot totally prevent the formation of SrZrO_3 second phase, was found to have delaminated after the same test.

9.3 Recommendations

1. Although the delamination problem could be prevented by adding dense GDC interlayer, performance of LSCF air electrodes still degrades during electrolysis test. This could be associated with the phase change and Sr surface segregation. Thus, it is important to figure out the exact mechanism and methods like surface modification can be explored to stabilize the performance.
2. In this work, all the experiments were performed on half-cells. However, in a half-cell, the so called electrolysis test is actually using the cell as an oxygen pump, not really an electrolyzer. Thus, some operating conditions, such as oxygen pressure distribution and current distribution, are slightly different from a full cell. More experiments are required to conduct on full cells in order to validate the mechanisms proposed in this work.
3. Other than improving the stability of LSCF air electrodes, efforts should also be put into searching other suitable air electrode materials. Currently, most of the work done are related to LSM- or LSCF-based air electrodes. However, lots of candidates can be explored to be used as stable air electrodes. In addition, model for the degradation phenomenon is critical to theoretically predict the stability of an air electrode.
4. It is well known that the degradation rate of a stack is much higher than a button cell. Thus, other than inspecting the degradation phenomenon on a half-cell, degradation caused by other components of a stack, interconnects

for instance, or by other factors like controlling strategy needs to be studied.

LIST OF RELATED PUBLICATIONS

Pan, Z., Liu, Q., Zhang, L., Zhang, X., & Chan, S. H. (2015). Effect of Sr Surface Segregation of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ Electrode on Its Electrochemical Performance in SOC. *Journal of The Electrochemical Society*, 162(12), F1316-F1323.

Pan, Z., Liu, Q., Zhang, L., Zhang, X., & Chan, S. H. (2016). Study of Activation Effect of Anodic Current on $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ Air Electrode in Solid Oxide Electrolyzer Cell. *Electrochimica Acta*, 209, 56-64.

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Under Review/Preparation

Pan, Z., Liu, Q., & Chan, S. H. Effect of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ air electrode-electrolyte interface on the short-term stability under high-current electrolysis in SOECs. *Under preparation*

Conference Contribution

Z. Pan, Q. Liu, S. H. Chan, Failure Mechanism of LSCF–YSZ Interface in SOEC Operated under High-Current Electrolysis. Fuel Cell Science and Technology 2016, Glasgow, UK. Oral Presentation

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